

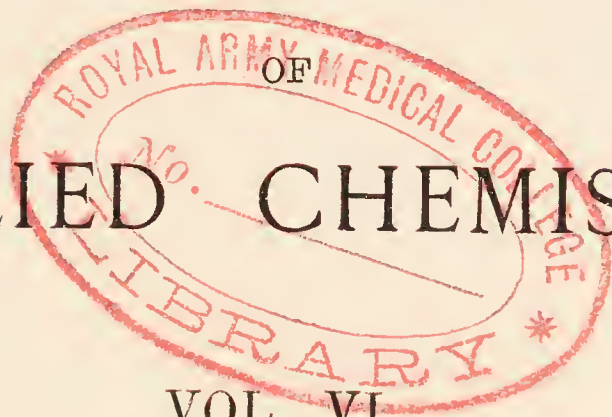
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A DICTIONARY
OF
APPLIED CHEMISTRY
VOL. VI.





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A DICTIONARY
OF
APPLIED CHEMISTRY

BY
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ASSISTED BY EMINENT CONTRIBUTORS



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On the much-lamented death of Sir Edward Thorpe, on February 23, 1925, it was found that much progress had been made with the two last volumes of his Dictionary. The final revision for the press has been carried out by H. Forster Morley, M.A., D.Sc., F.I.C., who was joint Editor of the last edition of Watts's "Dictionary of Chemistry," and Director of the "International Catalogue of Scientific Literature." It is hoped that Vol. VII., containing an Index to the whole work, will be published before the end of 1926.

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ABBREVIATIONS

OF THE TITLES OF JOURNALS AND BOOKS.

<i>Amer. Chem. J.</i>	American Chemical Journal.
<i>Amer. J. Pharm.</i>	American Journal of Pharmacy.
<i>Amer. J. Physiol.</i>	American Journal of Physiology.
<i>Amer. J. Sci.</i>	American Journal of Science.
<i>Amer. Min.</i>	American Mineralogist.
<i>Anal. Fis. Quim.</i>	Anales de la Sociedad Española Física y Química.
<i>Analyst</i>	The Analyst.
<i>Annalen</i>	Annalen der Chemie (Justus Liebig):
<i>Ann. Appl. Biol.</i>	Annals of Applied Biology.
<i>Ann. Chim. anal.</i>	Annales de Chimie analytique appliquée à l'Industrie, à l'Agriculture, à la Pharmacie et à la Biologie.
<i>Ann. Chim.</i>	Annales de Chimie.
<i>Ann. Falsif.</i>	Annales des Falsifications.
<i>Ann. Inst. Pasteur.</i>	Annales de l'Institut Pasteur.
<i>Ann. Physik.</i>	Annalen der Physik.
<i>Ann. Physique</i>	Annales de Physique.
<i>Ann. Report.</i>	Annual Reports of the Chemical Society.
<i>Annali Chim. Appl.</i>	Annali di Chimica Applicata.
<i>Apoth. Zeit.</i>	Apotheker-Zeitung.
<i>Arch. exp. Path. Pharm.</i>	Archiv für experimentelle Pathologie und Pharmakologie.
<i>Arch. Pharm.</i>	Archiv der Pharmazie.
<i>Astrophys. J.</i>	Astrophysical Journal.
<i>Atti R. Accad. Lincei</i>	Atti della Reale Accademia dei Lincei.
<i>Bentl. a. Trim.</i>	Bentley and Trimen. Medicinal Plants.
<i>Ber.</i>	Berichte der Deutschen chemischen Gesellschaft.
<i>Ber. Deut. pharm. Ges.</i>	Berichte der Deutschen pharmazeutischen Gesellschaft.
<i>Bied. Zentr.</i>	Biedermann's Zentralblatt für Agrikulturchemie und rationellen Landwirtschafts-Betrieb.
<i>Bio-Chem. J.</i>	The Bio-Chemical Journal.
<i>Biochem. Zeitsch.</i>	Biochemische Zeitschrift.
<i>Brewers J.</i>	Brewer's Journal.
<i>Brit. Assoc. Rep.</i>	Report of the British Association for the Advancement of Science.
<i>Brit. Med. J.</i>	British Medical Journal.
<i>Brit. Pat.</i>	British Patent.
<i>Bull. Acad. roy. Belg.</i>	Académie royale de Belgique—Bulletin de la Classe des Sciences.
<i>Bull. Asso. Chim. Sucr.</i>	Bulletin de l'Association des Chimistes de Sucrerie et de Distillerie.
<i>Bull. Imp. Inst.</i>	Bulletin of the Imperial Institute.
<i>Bull. Soc. chim.</i>	Bulletin de la Société chimique de France.
<i>Bull. Soc. chim. Belg.</i>	Bulletin de la Société chimique de Belgique.
<i>Bull. Soc. chim. Biol.</i>	Bulletin de la Société de chimie biologique.
<i>Bull. Soc. franç. Min.</i>	Bulletin de la Société française de Minéralogie.
<i>Chem. and Met. Eng.</i>	Chemical and Metallurgical Engineering.
<i>Chem. Ind.</i>	Chemische Industrie.
<i>Chem. News</i>	Chemical News.
<i>Chem. Soc. Proc.</i>	Journal of the Chemical Society of London. Proceedings.
<i>Chem. Soc. Trans.</i>	Journal of the Chemical Society of London. Transactions.
<i>Chem. Umschau.</i>	Chemische Umschau auf dem Gebiete der Fette, Öle, Wachse, und Harze.
<i>Chem. Weekblad</i>	Chemisch Weekblad.
<i>Chem. Zeit.</i>	Chemiker Zeitung.
<i>Chem. Zentr.</i>	Chemisches Zentralblatt.
<i>Compt. rend.</i>	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences.
<i>Dingl. poly. J.</i>	Dingler's polytechnisches Journal.
<i>D. R. P.</i>	Deutsches Reichs-Patent.
<i>Färber-Zeit.</i>	Färber-Zeitung.
<i>Flück. a. Hanb.</i>	Flückiger and Hanbury. Pharmacographia.
<i>Frld.</i>	Friedländer's Fortschritte der Teerfarbenfabrikation.
<i>Gazz. Chim. Ital.</i>	Gazzetta Chimica Italiana.
<i>Helv. Chim. Acta</i>	Helvetica Chimica Acta.
<i>J.</i>	Jahresbericht über die Fortschritte der Chemie und verwandter Theile anderer Wissenschaften.
<i>Jahrb. Min.</i>	Neues Jahrbuch für Mineralogie, Geologie und Palaeontologie.
<i>Japan J. Phys.</i>	Japanese Journal of Physics.

<i>J. Agric. Res.</i> . . .	Journal of Agricultural Research.
<i>J. Agric. Sci.</i> . . .	Journal of Agricultural Science.
<i>J. Amer. Chem. Soc.</i>	Journal of the American Chemical Society.
<i>J. Bact.</i>	Journal of Bacteriology.
<i>J. Bd. Agric.</i> . . .	Journal of the Board of Agriculture.
<i>J. Biol. Chem.</i> . . .	Journal of Biological Chemistry.
<i>J. Chem. Soc. Japan</i>	Journal of the Chemical Society of Japan.
<i>J. Chim. Phys.</i> . . .	Journal de Chimie Physique.
<i>J. Franklin Inst.</i> . .	Journal of the Franklin Institute.
<i>J. Gen. Physiol.</i> . .	Journal of General Physiology.
<i>J. Ind. Eng. Chem.</i>	Journal of Industrial and Engineering Chemistry.
<i>J. Inst. Brewing</i> . .	Journal of the Institute of Brewing.
<i>J. Pharm. Chim.</i> . .	Journal de Pharmacie et de Chimie.
<i>J. Pharm. Soc.</i>	
<i>Japan</i>	Journal of the Pharmaceutical Society of Japan.
<i>J. Phys. Chem.</i> . . .	Journal of Physical Chemistry.
<i>J. Physiol.</i>	Journal of Physiology.
<i>J. pr. Chem.</i>	Journal für praktische Chemie.
<i>J. Russ. Phys. Chem.</i>	
<i>Soc.</i>	Journal of the Physical and Chemical Society of Russia.
<i>J. Soc. Chem. Ind.</i>	Journal of the Society of Chemical Industry.
<i>J. Soc. Dyers.</i> . . .	Journal of the Society of Dyers and Colourists.
<i>J. Tokyo Chem. Soc.</i>	Journal of the Tokyo Chemical Society.
<i>J. Washington Acad.</i>	
<i>Sci.</i>	Journal of the Washington Academy of Sciences.
<i>Kolloid Zeitsch.</i> . .	Kolloid-Zeitschrift.
<i>Mem. Manchester</i>	
<i>Phil. Soc.</i>	Memoirs and Proceedings of the Manchester Literary and Philosophical Society.
<i>Met. & Chem. Eng.</i>	Metallurgical and Chemical Engineering.
<i>Min. Mag.</i>	Mineralogical Magazine and Journal of the Mineralogical Society.
<i>Monatsh.</i>	Monatshefte für Chemie und verwandte Theile anderer Wissenschaften.
<i>P.</i>	Proceedings of the Chemical Society.
<i>Pharm. J.</i>	Pharmaceutical Journal.
<i>Pharm. Zeit.</i> . . .	Pharmaceutische Zeitung.
<i>Phil. Mag.</i>	Philosophical Magazine (The London, Edinburgh and Dublin).
<i>Phil. Trans.</i>	Philosophical Transactions of the Royal Society.
<i>Phot. J.</i>	Photographic Journal.
<i>Physikal. Z.</i>	Physikalische Zeitschrift.
<i>Proc. Amer. Phil. Soc.</i>	Proceedings of the American Philosophical Society.
<i>Proc. K. Akad. Wetensch. Amsterdam</i>	Koninklijke Akademie van Wetenschappen te Amsterdam. Proceedings (English Version).
<i>Proc. Nat. Acad. Sci.</i>	Proceedings of the National Academy of Sciences.
<i>Proc. Physical Soc.</i>	Proceedings of the Physical Society of London.
<i>Proc. Roy. Irish Acad.</i>	Proceedings of the Royal Irish Academy.
<i>Proc. Roy. Soc.</i> . . .	Proceedings of the Royal Society.
<i>Proc. Roy. Soc. Edin.</i>	Proceedings of the Royal Society of Edinburgh.
<i>Rec. trav. chim.</i> . . .	Receuil des travaux chimiques des Pays-Bas et de la Belgique.
<i>Sci. Proc. R. Dublin Soc.</i>	Scientific Proceedings of the Royal Dublin Society.
<i>Sitz.</i>	Sitzungsberichte der K. Akademie zu Wien.
<i>Sitzungsber. Preuss. Akad. Wiss. Berlin</i>	Sitzungsberichte der Preussischen Akademie der Wissenschaften zu Berlin.
<i>Swiss Pat.</i>	Swiss Patent.
<i>T.</i>	Transactions of the Chemical Society.
<i>Trans. Faraday Soc.</i>	Transactions of the Faraday Society.
<i>U.S. Pat.</i>	United States Patent.
<i>Zeitsch. anal. Chem.</i>	Zeitschrift für analytische Chemie.
<i>Zeitsch. angew. Chem.</i>	Zeitschrift für angewandte Chemie.
<i>Zeitsch. anorg. Chem.</i>	Zeitschrift für anorganische Chemie.
<i>Z. Elektrochem.</i> . . .	Zeitschrift für Electrochemie.
<i>Z. ges. Brauw.</i>	Zeitschrift für das gesamte Brauwesen.
<i>Z. Kryst.</i>	Zeitschrift für Kristallographie.
<i>Z. Kryst. Min.</i>	Zeitschrift für Kristallographie und Mineralogie.
<i>Zeitsch. Nahr. Genussm.</i>	Zeitschrift für Untersuchung der Nahrungs- und Genussmittel.
<i>Z. Physik.</i>	Zeitschrift für Physik.
<i>Zeitsch. öffentl. Chem.</i>	Zeitschrift für öffentliche Chemie.
<i>Zeitsch. physikal. Chem.</i>	Zeitschrift für physikalische Chemie, Stöchiometrie und Verwandtschaftslehre.
<i>Zeitsch. physiol. Chem.</i>	Hoppe-Seyler's Zeitschrift für physiologische Chemie.

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A

DICTIONARY

OF

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S

S ACID. Peri acid. 1-naphthylamine-8-sulphonic acid; also applied to δ acid 1-naphthol-4:8-disulphonic acid and to 1:8-dihydroxy-naphthalene-4-sulphonic acid, and to 1-amino-8-naphthol-4-sulphonic acid.

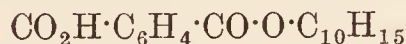
2-S ACID. 1-amino-8-naphthol-2:4-disulphonic acid.

SABADILLINE, SABADINE, SABADININE *v.* CEVADINE.

SABINENE *v.* TERPENES.

SABINOL $C_{10}H_{15} \cdot OH$ occurs in oil of savin, partly in the free state and partly as esters, from which it is obtained by hydrolysis (Fromm and Lischke, Ber. 1900, 33, 1202; Semmler, op. cit. 1462; Paolini and Rebora, Atti R. Accad. Lincei, 1916, [v.] 25, ii. 377; Henderson and Robertson, Chem. Soc. Trans. 1923, 123, 1713). It is an oil with b.p. 208° , sp.gr. $0.9483/20^{\circ}$, $0.9518/15^{\circ}$; μ_D 1.488; n_D^{18} 1.4895; $[\alpha]_D = +7^{\circ} 56'$.

The acetate $C_{10}H_{15} \cdot O \cdot C_2H_3O$ has b.p. 222° – 224° (Fromm, l.c.), the acid phthalate



forms colourless silky needles, m.p. 95° , $[\alpha]_D = -14^{\circ} 63'$ (in methyl alcohol).

Dihydrosabinol $C_{10}H_{18}O$, obtained by reduction of sabinol in presence of colloidal palladium, is a colourless liquid, b.p. 206° – 208° ; sp.gr. $0.9100/20^{\circ}$; μ_D 1.460, which may be further reduced by the xanthate method to α -thujene $C_{10}H_{16}$ (Henderson and Robertson, l.c.).

Other derivatives of sabinol are described by Fromm, Ber. 1898, 31, 2025; 1900, 33, 1191; Semmler, Ber. 1900, 33, 1455; Hämäläinen, Chem. Zentr. 1912, ii. 854; Biochem. Zeitsch. 1913, 50, 209.

Strychnine sabinol phthalate $C_{39}H_{40}O_6N_2$ crystallises in shining, white needles, m.p. 200° – 201° (Paolini and Rebora, Atti R. Accad. Lincei, 1916, [v.] 25, ii. 377).

SABROMIN. Trade name for the calcium salt of dibromobehenic acid, which is obtained by the action of bromine on erucic acid (*v.* SYNTHETIC DRUGS).

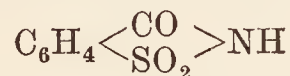
SACCHARANE is obtained by heating sugar *in vacuo* at 200° , and extracting the caramelised mass with methyl alcohol until the solvent is no longer coloured, treating the insoluble residue with water, and evaporating the solution *in vacuo*, after filtration. The yield is about 20 p.c. of the sugar taken. Saccharane, which has the formula $C_{12}H_{22}O_4 \cdot 2H_2O$, is not precipitated by lead acetate, is non-hygroscopic and tasteless. As its solution has a constant colouring power it has been proposed to employ it as the standard for determining the colour-value of commercial caramels by colorimetric methods (*v.* CAMEL) (Ehrlich, J. Soc. Chem. Ind. 1910, 506).

SACCHARETIN $(C_5H_7O_2)_x$, a term given by Langguth-Steuerwald (Chem. Zentr. 1912, i. 831) to the encrusting pigment of the sugar-cane with properties analogous to the phlobaphens. With phloroglucinol and hydrochloric acid, it gives an intense red coloration and with aniline sulphate and sulphuric acid, an orange colour. On dry distillation it yields pyrogallol; on warming with dilute acids, vanillic acid and vanillin are produced. On fusion with potassium hydroxide it yields protocatechuic acid and catechol.

SACCHARIC ACID *v.* CARBOHYDRATES.

SACCHARIMETRY *v.* SUGAR.

SACCHARIN (*o*-Benzoic sulphinide)



was discovered by Remsen and Fahlberg in 1879 (Ber. 12, 469; Amer. Chem. J. 1, 426), and was first prepared by Fahlberg on a large scale from coal tar or analogous substances containing a large proportion of toluene, benzene, &c.

Preparation.—Toluene, or the substance

containing it, is heated with fuming sulphuric acid, whereby *o*- and *p*-sulphonic acids



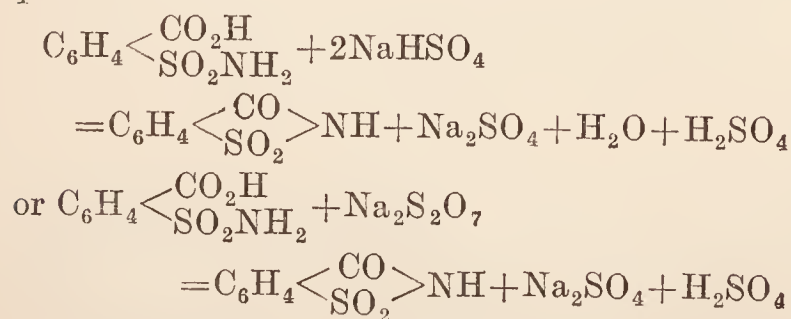
are formed. These are converted into their calcium salts by treatment with calcium carbonate and from the calcium salts the sodium salts are obtained. The latter are dried, and treated with phosphorus trichloride and a stream of chlorine, whereby two sulphonic chlorides are formed. The phosphorus oxychloride also formed is distilled off and the residue is strongly cooled and centrifugalised when the crystalline para-chloride separates from the ortho-chloride which is liquid. The latter is treated with dry ammonia or ammonium carbonate forming the amide $\text{CH}_3 \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_2\text{NH}_2$, which is washed with water and on oxidation with alkaline potassium permanganate yields the potassium salt of *o*-sulphamido-benzoic acid; the latter is treated with hydrochloric acid, forming the free acid $\text{CO}_2\text{H} \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_2\text{NH}_2$, which is spontaneously converted into saccharin (Eng. Pats. 6626, 1885; 22787, 1891; 10955, 1895; 17401, 1896; 9962, 1899; D. R. P. 122567). The mixture of ortho- and para-toluene sulphonic chlorides used may also be prepared by running one part of toluene into four parts of chloro-sulphonic acid at 0° (Monnet, Eng. Pat. 25273, 1924).

A number of other methods of preparing saccharin have been proposed.

100 lbs. of *o*-toluene sulphonamide may be mixed with 23 lbs. of slaked lime and stirred with 200 gallons of water. The mixture is heated to 70°–80°, and 180 lbs. of 98 p.c. calcium permanganate dissolved in 50 gallons of water are added gradually with constant stirring. The manganese compounds are removed by filtration and the saccharin is precipitated from the filtrate by addition of acid (Eng. Pats. 3563, 25481, 1903; see also Eng. Pats. 3680, 1898; 4525, 1900; 22214, 1901; U.S. Pat. 692863, 1902); or the *o*-toluene sulphonamide may be converted into saccharin by oxidising it electrolytically in the presence of alkaline permanganate at 40°–50° (Eng. Pat. 9322, 1903; see also Eng. Pat. 8661, 1895).

The methyl group in toluene may be oxidised to carboxyl before the introduction of the sulpho- or sulphamino- group, thus avoiding the formation and subsequent separation of *p*-toluene sulphonic chloride (Eng. Pat. 14122, 1906).

Saccharin may be manufactured by heating 10 parts of *o*-sulphamido-benzoic acid dissolved in 50 parts of alcohol with 40 parts of sodium bisulphate or 20 parts of sodium pyrosulphate for several hours on a water-bath with a reflux condenser when the following reaction takes place:—



The sulphuric acid is neutralised, the alcohol removed by distillation, when the residue con-

sists of saccharin and its ethyl ester, which is readily hydrolysed by sodium hydroxide at the ordinary temperature. The yield is said to be 95 p.c. of the theoretical (Eng. Pat. 7199, 1900; see also Eng. Pats. 3930, 1895; 21026, 1896; 1164, 15009, 1897; 19629, 1899; 12585, 1900).

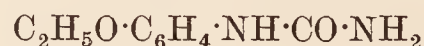
Saccharin has also been prepared from *o*-benzaldehyde sulphonic acid (Eng. Pat. 27655, 1896) and from *p*-bromacetanilide (Kreis, Annalen, 1895, 286, 377). For other methods, see Witting, Chem. Zeit. 11, 314; Eng. Pats. 5135, 1895; 1956, 1896; 10810, 1897; 6537, 1901; U.S. Pat. 692598, 1902; List and Stein, Ber. 1898, 31, 1665. Cf. Handbuch der Saccharin Fabrikation, by Dr. Oskar Beyer, Zurich, Rascher & Co. 1923.

Commercial saccharin generally contains a fairly large proportion of *p*-sulphamido-benzoic acid, the sweetening power of which is far less than that of saccharin. In addition it may contain ortho- and para-toluene sulphonamides or *o*-sulphamidobenzoic acid, toluene-2-4-disulphonamide and toluene-2-4-disulphonic acid, in greater or less quantity. The presence of certain of these impurities is indicated by incomplete solubility in an aqueous solution of sodium bicarbonate.

To purify it, hydrochloric acid sufficient to neutralise the *p*- salt is added to a concentrated solution of the alkali salts of crude saccharin. The para- acid separates, leaving the ortho- salt in solution which may now be treated with acid to obtain pure saccharin (Eng. Pats. 22787, 1891; 10769, 21417, 1903).

Saccharin is obtained in a very pure form by crystallisation from acetone, when it forms large, transparent monosymmetric crystals, which, when crushed, exhibit phosphorescence (Pope, Chem. Soc. Trans. 1895, 985).

Properties.—Saccharin is a white crystalline substance which, when quite pure, melts at 227°–227.5° corr. (small quantities of impurity cause considerable depression of the melting-point; cf. McKie, J. Soc. Chem. Ind. 1921, 150 T), and is 500 times as sweet as sugar (the commercial product is about 300 times as sweet), 1 part in 10,000 of water giving an intensely sweet taste. The sweetness of saccharin is increased by the addition of ‘*dulcin*,’ para-phenetole carbamide



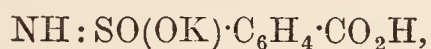
which, by itself, has a lower sweetening property. A mixture of 280 mg. of saccharin and 120 mg. of dulcin dissolved in 1 litre of water has the same sweetness as 535 mg. of saccharin dissolved in 1 litre of water (Paul, Chem. Zeit. 1921, 45, 38). Saccharin sublimes at 100° and is soluble in cold water only to the extent of 1 in 400, in boiling water 1 in 28, in alcohol 1 in 30, in glycerol and in amyl acetate 1 in 50, in ethyl acetate 1 in 20. It is also soluble in ether, in ammonia, and in alkali carbonate solutions, the alkali salts being formed in the latter case. It is not attacked by nascent hydrogen in alkaline solutions, by potassium permanganate, by hydrogen peroxide or by halogens or nitric acid in the cold. With hot nitric acid it is hydrolysed.

From a consideration of the sweetness of various derivatives of ‘saccharin,’ O. J. Magidson and S. W. Gorbatschov (Ber. 1923 56,

[B] 1810–1817) draw the conclusion that it is the 'saccharin' ion and not the molecule which causes its solutions to have a sweet taste. It is shown that, in accordance with this view, its sweetening power and molecular conductivity are affected very similarly by dilution. Similarly, the sweetness of 'sodium-saccharin,' or 'crystallose' is depressed in the presence of other sodium ions, exactly as would be expected in accordance with theory.

'*N*-saccharinacetic acid' (*o*-benzoicsulphinidoacetic acid) is prepared by the action of ethyl chloroacetate on 'sodium-saccharin,' and crystallises in needles, m.p. 212°–215°. It has a bitter, acid taste, and its dissociation constant ($k=0.14 \times 10^{-4}$) is practically that of acetic acid (Magidson and Gorbatschov, *l.c.*; J. Chem. Soc. Abstr. 1923, 124, i. 1097–1098).

When boiled with hydrochloric acid saccharin forms *o*-sulphamido-benzoic acid, and then ammonium hydrogen sulphobenzoate $\text{CO}_2\text{H} \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_3\text{NH}_4$ (Remsen and Burton, Amer. Chem. J. 11, 403). Treated with a mixture of hydrochloric acid and potassium chlorate (nascent chlorine) it forms, first, potassium *o*-iminosulphobenzoic acid



transparent tabular rhombic crystals, m.p. 285°–286°, and, secondly, *o*-chlorobenzoic acid (Bertolo, Gazzetta, 1911, 41, i. 698).

Saccharin acts as a disinfectant, but as a preservative for beer it is said to be practically useless (Burkard and Seifert, Chem. Zeit. 1895, 19, 220; Machledeit, Wochenschr. Brauerei, 1898, 15, 365). For the toxicity of saccharin, see Warschaffelt (Pharm. Weekblad, 1915, 52, 37).

Saccharin is used as a sweetening agent, particularly in the manufacture of sweetened aerated waters (Chem. Zeit. 12, 106; Bull. Soc. chim. 1889, 348; Levinstein, J. Soc. chem. Ind. 1886, 75), although its use in food is prohibited in some countries. It is employed in medicine as a substitute for sugar in diabetes, liver disease, for the reduction of corpulence, and generally where the use of sugar is undesirable, and it may be mixed with alkaloids to render their taste less objectionable (Eng. Pat. 596, 1886).

According to Nencki (Chem. Zeit. Rep. 1899, 23, 372), and to Berlioz (*ibid.* 1900, 24, 416), the effect of saccharin on the digestion is less than that of an equivalent weight of sugar. This opinion is, however, contrary to the widely accepted view and is, according to Windisch (Wöch. Brau. 1900, 17, 284), based on essentially incorrect assumptions (see also Chassevant, Compt. rend. Soc. Biol. 1901, 53, 206; J. Soc. Chem. Ind. 1886, 421; *ibid.* 1882, 292, 688; *ibid.* 1889, 66; *ibid.* 1890, 545, 1062; Thümen, Chem. Zeit. 1891, 15, 634).

The prevailing view that, except for its action on the organs of taste in the mouth, saccharin is an inert substance, having no action on organs and tissues, is not tenable. Acting in the mouth, it decreases appetite, gastric secretion, and peptic digestion. Acting in the small intestine, it decreases absorption; on the erythrocytes, it decreases hæmolysis. These actions cannot be explained by the osmotic factor. Saccharin in the blood, in proportion to

its concentration, passes into the lymph, cerebrospinal fluid, saliva, tears, and mammary secretion (A. J. Carlson and others, J. Metabol. Research, Morristown, N.Y., March, 1923, 451; through J. Amer. Med. Assoc., Nov. 3, 1923, 1558; Pharm. J. 1923, iii. 620).

Tests.—Saccharin gives a voluminous precipitate with mercurous nitrate and a less abundant precipitate soluble in excess with mercuric nitrate (Parmeggiani, Bull. chim. Farm. 1908, 47, 37). When saccharin is heated with sulphuric acid and diresorcinol a product is obtained which when treated with water and filtered forms an intensely violet liquid (Wauters, J. Soc. Chem. Ind. 1909, 733). When saccharin is evaporated to dryness with nitric acid, cooled, and a few drops of a solution of sodium hydroxide in 50 p.c. alcohol is added, a faint yellow colour is formed. If the liquid is spread out on the surface of the dish and heated rapidly, blue-violet and red streaks are formed (Lindo, Chem. News, 1888, 58, 51, 155). Saccharin gives the usual test for sulphur in organic compounds. To carry this out the substance containing saccharin is evaporated to dryness and transferred to a small reduction tube in which a small piece of sodium or potassium has been placed. The whole is heated, and when the reaction is over, the tube, whilst still hot, is immersed in freshly prepared sodium nitroprusside when a violet colour will be produced—salicylic acid does not interfere with this test (Mahler, Chem. Zeit. 1905, 29, 32). Saccharin gives a bright red coloration when 0.1 gram dissolved in 25 c.c. of water is treated with 10 c.c. of 0.1 p.c. sodium nitrite solution, 6 drops of dilute sulphuric acid and, after a few minutes, 0.1 gram of β -naphthol (Thevenon, J. Pharm. Chim. 1920, vii. 22, 421).

The substance is evaporated almost to dryness in a porcelain crucible, and the residue, after being treated with a drop or two of water and a particle of caustic soda, is again evaporated to dryness and fused. The cold mass is dissolved in 1 c.c. of water, neutralised with dilute acid and tested with 1 p.c. ferric alum reagent, when, if saccharin is present, a violet colour is produced (Geuth, Amer. J. Pharm. 1909, 81, 536; see also Truchon, Chem. Zentr. 1900, i. 691; Brévans, *ibid.* 1105; Villiers, *ibid.* 1904, i. 1457; Chase, J. Amer. Chem. Soc. 1904, 26, 1627; Durand, J. Ind. Eng. Chem. 1913, 5, 987).

If salicylic acid is present it has to be removed before this test can be applied; for this purpose the solution is mixed with hydrochloric acid and bromine water is added in excess, this precipitates the salicylic acid quantitatively. The solution is then filtered and excess of bromine is removed by a current of air (Hairs, Chem. Zentr. 1893, ii. 987; Bonamartini, Rev. Intern. Falsif. 1906, 19, 39).

When saccharin is heated with a small quantity of a mixture of 5 c.c. of phenol and 3 c.c. of strong sulphuric acid for 5 mins. at 160°–170°, and the product is dissolved in water, on addition of a solution of sodium hydroxide, the solution becomes purple-red or rose-red according to the amount of saccharin present: salicylic and benzoic acids do not interfere with this reaction. Other phenols also give characteristic colours (Kastle, Chem. Zentr. 1906, i. 1575).

0.01 to 0.02 gram of the substance is dissolved in 10 c.c. of water and made faintly alkaline. A solution of diazotised *p*-nitraniline is added drop by drop with agitation until the colour first formed disappears. The liquid is then shaken with ether and the lower layer is withdrawn and replaced by 20–30 drops of 10 p.c. caustic soda solution. On gentle agitation a green ring is formed in the presence of saccharin, a red one in that of salicylic acid, and a red-brown ring in the presence of both. If the soda is removed and replaced by ammonia, the ether is decolorised and the ammonia becomes blue-green in the first case, red in the second, and violet in the third case (Riegler, Chem. Zentr. 1900, ii. 880; 1901, i. 66).

Saccharin may be determined microchemically by means of nitron, if the former be first converted into *o*-sulphamido-benzoic acid by treatment with dilute alkali (Visser, Chem. Zentr. 1907, i. 302).

To detect saccharin in beer, wines, syrups, &c., the bitter principle of hops must first be removed by treatment with copper nitrate until no further precipitate is formed. The solution is then mixed with pure sand and phosphoric acid, and after concentration is extracted with a mixture of ether and light petroleum. The extract is evaporated and the residue is dissolved in a little sodium carbonate solution, and is tested by the taste and other methods as above. If the substance contains tannin this may be removed by the addition of ferric chloride, after which the solution is made slightly alkaline by addition of calcium carbonate. Cf. also Ledent, Ann. Chim. anal. 1913, 18, 314; Karas, Zeitsch. Nahr. Genussm. 1913, 25, 559; Condelli, Ann. Chim. Anal. 1915, 20, 44.

The solution of the food or beverage may be freed from alcohol by evaporation and acidified with acetic acid (20 drops for every 100 c.c.); it is then treated with a normal solution of lead acetate in excess and allowed to stand for 30 minutes, after which excess of N/5 solution of sodium sulphate containing an equal quantity of sodium phosphate is added and the lead salts are removed by filtration. The filtrate is concentrated on the water-bath, acidified with dilute sulphuric acid and shaken with a mixture of equal volumes of ether and benzene. The extract after evaporation may now be treated with potassium permanganate and sulphuric acid to oxidise the salicylic acid, and the product again extracted with ether and benzene. The evaporated extract is then examined as above (Bianchi and Nola, J. Soc. Chem. Ind. 1909, 1267; Jörgensen, *ibid.* 732; Pawlowski, *ibid.* 732; Karas, Zeitsch. Nahr. Genussm. 1913, 25, 559).

For other methods of detecting saccharin in beverages, see Spaeth, Zeitsch. angew. Chem. 1893, 579; Wauters, Chem. Zentr. 1896, i. 576; Morpurgo, *ibid.* 1897, ii. 531; Rossing, *ibid.* 1899, ii. 274; Herzfeld and Wolff, Wochenschr. Brau. 1898, 15, 335, 608; Wirthle, Chem. Zeit. 1900, 24, 1035; Blarez, Bull. l'Assoc. Chim. Sucr. Dist. 1899, 17, 319; Boucher and Bounge, Bull. Soc. chim. 1903, [iii.] 29, 411; Spica, Gazz. chim. ital. 1901, 31, ii. 41; Tagliavini, Boll. Chim. Farm. 1907, 46, 645.

To detect saccharin in foods rich in proteids, fats, and starch, the substance, mixed with sand

and slaked lime, may be extracted with a mixture of alcohol and sodium chloride solution. The fat is then removed from the extract by light petroleum, and the remaining liquid is freed from alcohol by evaporation on a water-bath, cooled, extracted with ether to remove dulcin, again evaporated and acidified with sulphuric acid, after which the saccharin is extracted with a mixture of ether and light petroleum (Tortelli and Piazza, Zeitsch. Nahr. Genussm. 1910, 20, 489; Camilla and Pertusi, Chem. Zentr. 1911, ii. 1269; Bonis, Ann. Falsif. 1917, 10, 210; 1918, 11, 369; Analyst, 1917, 303; Durand, J. Ind. Eng. Chem. 1913, 5, 987; Condelli, Ann. Chim. anal. 1915, 20, 40; Klostermann and Scholta, Zeitsch. Nahr. Genussm. 1916, 31, 67).

For the detection of saccharin and dulcin in vinegar or foodstuffs containing vinegar, see G. Reif, Zeitsch. Unters. Nahr. Genussm. 1923, 46, 217.

Determination of dulcin (in foodstuffs) by means of xanthidrol.—According to G. Reif (Zeitsch. Unters. Nahr. Genussm. 1924, 47, 238) dulcin forms a crystalline condensation product with xanthidrol analogous to that formed by urea. Xanthidulcin crystallises from acetone in fine needles (m.p. 246°), and is soluble in hot amyl alcohol, acetone, and toluene. It is sparingly soluble in hot and cold water, methyl and ethyl alcohols, chloroform, ether, ethyl acetate, petroleum spirit, and benzene. Dulcin is almost quantitatively transformed into xanthidulcin when its solution in a mixture of 20 c.c. of glacial acetic acid and 20 c.c. of water is treated with 0.2 gram of xanthidrol dissolved in 3 c.c. of anhydrous methyl alcohol for 2 hours at the ordinary temperature. The majority of substances usually present in foodstuffs have no disturbing effect on this reaction. Substances such as ureas, amides, and allantoin, which also form insoluble compounds with xanthidrol, may be removed during the process of isolating the dulcin. The method described includes purification with normal lead acetate, treatment with sodium hydroxide, and extraction of the dulcin with ethyl acetate. Saccharin also forms an insoluble compound with xanthidrol, but not in quantitative yield under the conditions found most suitable for dulcin. It must therefore be removed by the extraction of the alkaline solution with ethyl acetate, in which the saccharin compound is insoluble. The accuracy of the method for the determination of dulcin in foodstuffs is established by the results of determinations on starch syrup, fruit juices and wines, liqueurs, and mustard, all of which gave good results (J. Soc. Chem. Ind. 1924, 43, B. 571).

For the detection of saccharin in milk and butter, see also Leys, Compt. rend. 1902, 132, 1056; Wirthle, Chem. Zeit. 1901, 25, 816; Formenti, Chem. Zentr. 1902, ii. 541.

For the detection and estimation in cocoa powders, see Driessen Mareeuw, Pharm. Weekblad. 1907, 44, 245; Ceccherelli, Boll. Chim. Farm. 1915, 54, 641.

Saccharin may be estimated by the following process:—

0.5–1 grm. of saccharin or saccharin mixture is weighed into a 100–120 c.c. glass flask and 50 c.c. of N/1 (better 1.5 N), HCl is added. The

flask, fitted with an air condenser, is boiled gently for $2\frac{1}{2}$ hours (better 4 hours), the ammonia produced is estimated by Kjeldahl's process, and the number of c.c. N/10 sulphuric acid used to neutralise the ammonia multiplied by 0.0183 gives the weight in grams of pure saccharin present in the sample (Proctor, Chem. Soc. Trans. 1905, 242; Testoni, Zeitsch. Nahr. Genusssm. 1909, 18, 577; Bonis, Ann. Falsif. 1918, 11, 369). Pure saccharin should yield 7.65 p.c. of ammonia. Richmond and Hill (J. Soc. Chem. Ind. 1918, 248 T; 1919, 38, 8 T) treat the saccharin with 10 c.c. of 7.5 N sodium hydroxide, boil for 2 minutes, cool, add 15 c.c. of 10 N hydrochloric acid (B. P. strength) and boil for 50 minutes under a reflux condenser; after cooling 75 c.c. of cold water is added, a current of air passed through the upper part of the flask to remove acid vapours, 15 c.c. of 7.5 N sodium hydroxide solution added and the ammonia distilled off into 20 c.c. of N/5 hydrochloric acid. When about 70 c.c. has been distilled the solution is titrated with N/10 alkali using methyl red preferably as indicator. With 0.6104 grm. of saccharin the number of c.c. of N/10 acid neutralised multiplied by 3 = percentage of saccharin. For further details, see J. Soc. Chem. Ind. 1919, 8 T. According to O. Beyer (Chem. Zeit. 1919, 43, 537; 1920, 44, 437) of the methods which have been proposed for the estimation of saccharin only two are trustworthy, viz. the hydrolytic method and that described by Richmond and Hill. When the m.p. of a sample of saccharin falls below 220° , the amount of *p*-sulphonamido-benzoic acid present should be determined by heating 1 grm. of the sample for 2 hours under a reflux condenser with 10 c.c. of hydrochloric acid (sp.gr. 1.12) and 10 c.c. of water, filtering if necessary, evaporating to dryness, dissolving in 10 c.c. of hot water, and collecting, drying, and weighing the crystals after standing for at least 12 hours. Study of the melting-point curves of mixtures of saccharin with *o*- and *p*-sulphamidobenzoic acids and *o*-toluene sulphonamide shows that the melting-point is a safe guide to the percentage composition of mixtures up to 10 p.c. in the case of the para-acid (m.p. 288° – 289° corr.) and the ortho-amide. Mixtures with the ortho-acid cannot be estimated by the melting-point, as this acid decomposes at 180° (McKie, J. Soc. Chem. Ind. 1921, 40, 150 T). An investigation by O. Beyer (Chem. Zeit. 1923, 47, 744) into the degree of accuracy of methods of determining the *p*-sulphamidobenzoic acid in commercial and technical saccharins showed that the German official method is capable of determining quantities of 1 p.c. and upwards when 10 grms. of the sample is taken for analysis, and may be considered sufficiently accurate for practical purposes. Hefelmann's method does not give such good results, and is not so convenient, because the saccharin does not dissolve so readily in the 73 p.c. sulphuric acid prescribed as in the 25 p.c. hydrochloric acid prescribed in the official method (J. Soc. Chem. Ind. 1923, 42, 1043, A). Saccharin may also be estimated as mercury saccharinate ($\text{C}_6\text{H}_4[\text{COSO}_2]_2\text{N}_2\text{Hg}$) by precipitating with mercury nitrate (Vitali, Chem. Zentr. 1899, i. 1297). It may also be estimated by converting it into

salicylic acid (Schmidt). For other methods, see Delle, *ibid.* 1900, ii. 744; Défournel, J. Pharm. 1901, [iv.] 13, 512; Parmeggiani, *l.c.*; Pazienti, Ann. Chim. Applicata, 1914, 2, 290; Ceccherelli, Boll. chim. farm. 1915, 54, 641; in urine and faeces, Bloor, J. Biol. Chem. 1910, 8, 227; Wakeman, *ibid.* 233; Klostermann and Scholta, Zeitsch. Unters. Nahr. Genusssm. 1916, 31, 67; Analyst, 1916, 309; Gnaedinger, J. Assoc. Off. Agric. Chem. 1917, 5, 25; Analyst, 1917, 304; G. S. Jamieson, J. Biol. Chem. 1920, 41, 3.

The chief impurity in commercial saccharin, *p*-sulphamidobenzoic acid, may be estimated in the absence of other impurities by titration with N/10 caustic soda (Glückmann, Chem. Zentr. 1901, ii. 588; see also Reid, Amer. Chem. J. 1899, 21, 461; J. Soc. Chem. Ind. 1900, 860).

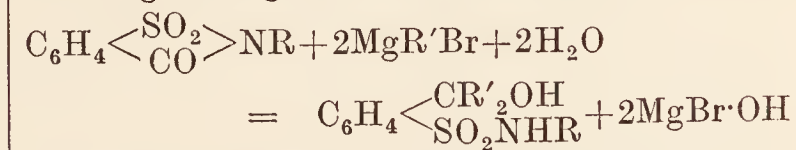
DERIVATIVES OF SACCHARIN.

Saccharin combines with mineral and organic bases, forming well-defined, usually crystalline salts which may be obtained by the action of carbonates or bicarbonates on saccharin or by the action of sulphate on *sodium saccharinate*, which is very soluble in water and is known as *soluble saccharin*. The latter is often used instead of saccharin, both in medicine and for sweetening purposes (Chemist and Druggist, 32, 642).

Sucramine, the ammonium salt, is formed by dissolving saccharin in the required amount of ammonia. After standing for some time, the solution deposits white crystals far sweeter than saccharin, being 700 times as sweet as cane-sugar. It melts at about 150° , is equally soluble in hot and cold water, and is also soluble in methyl and ethyl alcohol, but not in other organic solvents (Défournel, Bull. Soc. chim. 1901, 25, 322; Bellier, Chem. Zentr. 1901, i. 423; Blarez, Zeitsch. Nahr. Genusssm. 1901, 4, 763). Other metallic derivatives are also known.

Alkyl derivatives of saccharin of the type $\text{C}_6\text{H}_4\langle\text{SO}_2\rangle\text{NR}$ are obtained by the interaction of the sodium salt and the required alkyl iodide (Fahlberg and List, Ber. 1887, 20, 1596; Brackett, Amer. Chem. J. 9, 406).

Ethyl-saccharin (Sachs, Wolff and Ludwig, Ber. 1904, 37, 3252) forms long needles, m.p. 96° – 97° , is tasteless and readily soluble in hot water. Like other alkyl saccharins it combines with organomagnesium bromide thus:—



Methyl-saccharin forms flat needles, m.p. 131° – 132° . Methyl-saccharin of formula

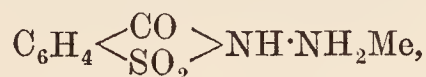


is formed by converting *p*-toluidine-*m*-sulphonic acid into the corresponding cyano-toluene sulphonic acid by the diazo-reaction. By the action of ammonia, the cyano-sulphamide is obtained, and this by hydrolysis yields the acid $\text{C}_6\text{H}_3\text{Me}(\text{SO}_2\text{NH}_2)\text{CO}_2\text{H}$, which on heating yields methyl-saccharin (D. R. P. 48583). It melts at 246° , resembles saccharin in taste, is readily

soluble in hot, sparingly so in cold, water, and is soluble in alkalis and many organic solvents. A number of derivatives of methyl-saccharin have been obtained (Weber, Ber. 1892, 25, 1737).

Ethoxy-saccharin $\text{OEtC}_6\text{H}_3\langle\text{SO}_2\rangle\text{NH}$, has m.p. $257^\circ\text{--}258^\circ$, and is not sweet (Remsen and Palmer, Amer. Chem. J. 1886, 8, 227).

Saccharinate of monomethylamine



m.p. $156.5^\circ\text{--}157^\circ$, is prepared by mixing aqueous solutions of methylamine and saccharin in equimolecular proportions and evaporating the mixture *in vacuo*. Salts of saccharin with other amines are prepared similarly. They are very soluble in water and in alcohol, but are insoluble in most organic solvents (Fr. Pat. 322096, 1902; Eng. Pat. 12181, 1902).

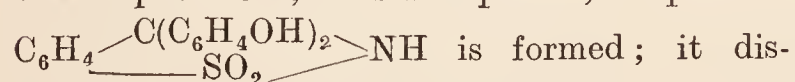
Saccharin reacts with phenylcarbazine, forming a compound which crystallises in white needles, m.p. 98° , and is decomposed by dilute sulphuric acid or by prolonged boiling with water with formation of *o*-sulphamidobenzoic acid (Défournel, Bull. Soc. chim. 1901, [iii.] 25, 604).

Nitro-, amino-, and alkylnitro-, amino- and carboxylic derivatives of saccharin have been prepared (Noyes, Amer. Chem. J. 8, 167; Remsen and Gray, *ibid.* 1897, 19, 496; J. Soc. Chem. Ind. 1889, 476; Eckenroth and Koerppen, Ber. 1896, 29, 1048; *ibid.* 1897, 30, 1265; Zincke and Schürmann, Ann. 1918, 416, 65).

When chlorine is passed into a potash solution of saccharin the products formed depend on the quantity of alkali present. If an equivalent amount of saccharin is used, the sparingly soluble *chloride* $\text{C}_6\text{H}_4\langle\text{CO}\rangle\text{SO}_2\text{NCl}$, m.p. 152° , separates. This substance is not sweet, is similar in taste to a hypochlorite and in odour to chloral. If excess of alkali is present, the solution remains clear, and if an acid is added a precipitate is formed which may be *o*-sulphon-chloramidobenzoic acid or *o*-sulphondichloramidobenzoic acid or a mixture of both, depending on the quantity of chlorine used (Chattaway, Chem. Soc. Trans. 1905, 1882).

Saccharin forms a white waxy condensation product with formaldehyde (Parmeggiani, *l.c.*). It also combines with caffeine, strychnine, quinoline, piperazine, phenetidine, and antipyrin, forming products which are said to be useful as antiseptics and anti-fermentatives (Eng. Pat. 25152, 1899).

Saccharin condenses with phenols, forming products of a constitution similar in type to that of phthalein; thus with phenol, the product



is formed; it dissolves in alkalis giving a red solution, which is decolorised on addition of acids. With resorcinol, a brown-red mass is obtained which forms an orange-yellow solution in alkalis. When diluted, the solution exhibits a powerful green fluorescence. The colouring matter is precipitated by acids and may be purified by dissolving it in alcohol and precipitating with water. It forms a brown resin with a metallic lustre and yields a *triacetyl-* derivative, m.p. 286° , which,

on saponification, yields the pure *sacchareïn* $\text{SO}_2\langle\text{NH}\rangle\text{C}\langle\text{C}_6\text{H}_3\text{OH}\rangle\text{O}$. The latter crystallises in salmon coloured scales, m.p. $265^\circ\text{--}267^\circ$, soluble in water, alcohol, and in alkalis, forming in the latter a pure yellow solution with a green fluorescence. It yields halogen derivatives which also form coloured solutions in alkalis. The sacchareïns of ethyl- and methylmetamino-phenols also form colouring compounds (Monnet, and Kœtschet, Bull. Soc. chim. 1897, [iii.] 17, 690, 1030; Sisley, *ibid.* 821). The latter, although very similar to the rhodamines in colouring and general properties, are instantly decolorised by alkalis, but if an acid radicle is introduced in the imido-group, the colouring matters formed are among the most stable towards alkalis. See also Dutt, Chem. Soc. Trans. 1922, 121, 2389.

Phosphorus pentasulphide acts upon saccharin at 220° , yielding *thio-o-benzoicsulphinide* $\text{C}_6\text{H}_4\langle\text{CS}\rangle\text{SO}_2\text{NH}$, yellow needles, m.p. 180° (Mannessier, Gazz. chim. ital. 1915, 45, i. 540).

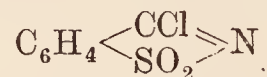
Saccharin on treatment with sodium and amyl alcohol loses its imino-group as ammonia; the sulphonic group is also detached, and after acidification is liberated as sulphur dioxide, the final product of the reaction being hexahydrobenzoic acid (Gianformaggio, Gazz. chim. ital. 1920, 50, i. 327).

Pseudo - saccharin $\text{C}_6\text{H}_4\langle\text{C}(\text{OH})\rangle\text{SO}_2\text{N}$ or $\text{C}_6\text{H}_4\langle\text{C}(\text{NH})\rangle\text{SO}_2\text{O}$ is formed by heating equi-

molecular proportions of sulphobenzoic acid and acetonitrile at $165^\circ\text{--}170^\circ$ for 5 hours. The product is extracted with alcohol, and on evaporation of the latter, the ψ -saccharin separates as minute white crystals, m.p. 225° . They dissolve readily in water and in alcohol, not in ether, and are not sweet (Mathews, J. Amer. Chem. Soc. 1898, 20, 662).

Many derivatives of ψ -saccharin have been prepared (Jesurun, Ber. 1893, 26, 2286; Remsen, *ibid.* 2643; Fritsch, *ibid.* 1896, 29, 2295; Bradshaw, Amer. Chem. J. 1906, 35, 335; Schrader, J. pr. Chem. 1917, (ii) 95, 312).

Chloro- ψ -saccharin (*chlorobenzalsultim*)



is prepared by passing chlorine into an aqueous solution of saccharin. It forms white crystals, m.p. 170° , only sparingly soluble in most organic solvents and is converted by alcohol into *ethoxy- ψ -saccharin* (*ethoxybenzalsultim*) (Maselli, Gazz. chim. ital. 1900, 30, ii. 529; Fritsch, Ber. 1896, 29, 2290).

For other halogen derivatives, see Roode, Amer. Chem. J. 13, 217; Brackett, *l.c.*; Holleman, Rec. trav. chim. 1906, [ii.] 25, 330.

SACCHARINIC ACID $\text{C}_6\text{H}_{12}\text{O}_6$. An unstable acid obtained as the calcium salt by boiling solutions of dextrose ($\text{C}_6\text{H}_{10}\text{O}_5$) with freshly precipitated chalk (Scheibler, Ber. 1880, 13, 2212; Kiliani, Annalen, 1883, 218, 373; Liebermann and Scheibler, Ber. 1883, 16, 1821; Hermann and Tollens, *ibid.* 1884, 17, 1333). *Iso-* and *metasaccharinic acids* are formed as calcium salts by the action of lime on milk-sugar. The former is also formed

by boiling oxycelluloses with milk of lime (Faber and Tollens, Ber. 1899, 32, 2596). The latter may be prepared by treating galactose with water and freshly precipitated calcium hydroxide (Kiliani and Sandra, Ber. 1893, 26, 1650).

Para-saccharinic acid is also formed in the preparation of the *meta-* acid by the last method.

Both the *meta-* and the *para-* acids are readily converted into the same pentose—an aldose which when oxidised with bromine yields a butanetriolcarboxylic acid (Kiliani, Ber. 1908, 41, 120).

Literature on the saccharinic acids and their derivatives: Lobry de Bruyn and von Ekenstein, Ber. 1895, 28, 3078; Fischer and Passmore, Ber. 1889, 22, 2728; Sorokin, J. pr. Chem. [ii.] 37, 318; Kiliani and Loeffler, Ber. 1904, 37, 1196; Kiliani, *ibid.* 1908, 41, 158, 469; Rimbach and Heiten, Annalen, 1908, 359, 317; Nef, *ibid.* 1910, 376, 1.

SACCHARINS *v.* CARBOHYDRATES.

SACCHARONE $C_6H_8O_6 \cdot H_2O$. A substance obtained by the action of nitric acid on saccharin (Kiliani, Ann. 1883, 218, 149).

SACRED BARK *v.* CASCARA SEGRADA.

SAFETY EXPLOSIVES *v.* EXPLOSIVES.

SAFFLORITE *v.* SMALTITE.

SAFFLOWER (*bastard saffron*). This dye-stuff consists of the dried florets of *Carthamus tinctorius* (Linn.), an annual thistle-like plant belonging to the *Cynarocephalæ*. A native of Southern Asia, it has been cultivated in China, India, Persia, Egypt, also in central and southern Europe. When in full bloom the yellow florets are plucked, and either at once dried, so as to form an orange-coloured fibrous mass somewhat resembling saffron, or they are first kneaded with water, in order to remove a useless yellow colouring matter, and then pressed into the form of lens-shaped cakes and dried.

Safflower owes its value to an insoluble red colouring matter which occurs only in very small amount, about 0.5 p.c., whereas the soluble yellow colouring matter is said to be present to the extent of about 30 p.c.

The yellow colouring matter may be obtained by first precipitating a cold aqueous extract of safflower with lead acetate and acetic acid and then adding ammonia to the filtrate, *i.e.* precipitating with basic lead acetate. The yellow precipitate thus obtained is carefully decomposed with dilute sulphuric acid, and after removing the lead sulphate the filtrate is evaporated to dryness with exclusion of air. It is thus obtained as an amorphous substance, having acid properties, a bitter taste, and a peculiar odour. It is of a very unstable character, and on exposure to air seems to oxidise, becoming brown and somewhat insoluble in water. According to Schlieper, its composition is represented by the formula $C_{16}H_{20}O_{10}$; according to Malin, it is $C_{24}H_{30}O_{15}$. This product is apparently a glucoside or contains a substance of this character, for after digestion with boiling dilute sulphuric acid, the solution yields to ether a small quantity of a crystalline yellow colouring matter (private communication).

Carthamin or *carthamic acid* is the name given to the useful red colouring matter, which, although insoluble in water, is readily soluble in alkaline solutions. To obtain it, safflower is

well washed with slightly acidified water to remove the yellow colouring matter, then it is steeped for some time in a cold dilute solution of sodium carbonate. If the alkaline solution be now acidified with acetic or tartaric acids the carthamin is precipitated in so finely divided a condition that it cannot be successfully collected. This difficulty is, however, obviated by making use of the fact that carthamin is readily attracted and removed from its acidified solution by cellulose. Hence bleached cotton is immersed and moved about in the alkaline solution, which is at the same time gradually acidified with tartaric or citric acid.

In this manner the carthamin is slowly precipitated and is at once attracted by the cotton, which thus becomes dyed red. After washing the dyed cotton with slightly acidified water, the colouring matter is dissolved off by means of a dilute solution of sodium carbonate, from which the carthamin is thrown down, on the addition of tartaric acid, as a bright-red precipitate, which is now in a purer and more granular form. Further purification is effected by dissolving the dried precipitate in alcohol and reprecipitating with water.

Preisser, the first to investigate carthamin (J. pr. Chem. 1844, [i.] 32, 142), described this substance as colourless needles, which, by air-oxidation in the presence of alkali, were converted into carthamein, the true colouring matter. Schlieper (Annalen, 1846, 58, 357), however, proved that Preisser's statements were incorrect, and he isolated carthamin in the form of green, iridescent, red crusts, or as a granular, greenish-red powder, to which he assigned the formula $C_{14}H_{14}O_7$. When digested with boiling alcohol, it was converted into a yellow compound having the composition $C_{14}H_{14}O_9$. According to Malin (Annalen, 1840, 36, 117), carthamin gives *p*-hydroxybenzoic acid when digested with boiling potassium hydroxide solution.

Radcliffe (J. Soc. Dyers, 1897, 13, 158), by extracting an air-dried commercial paste extract of safflower with methyl alcohol, subsequently evaporating the solution, and adding hot water, obtained a product crystallising in red, iridescent needles, melting at 168°–169° (provisional), which, when exposed to sunlight, changed to a red powder. According to Kametaka and Perkin, this product is a salt of carthamin rather than the colouring matter itself.

Kametaka and Perkin (Chem. Soc. Trans. 1910, 97, 1415) have prepared carthamin in a crystalline condition. The dried and finely-ground commercial extract of safflower is extracted on the water-bath with successive quantities of pyridine, and the combined extracts are evaporated to a small bulk under reduced pressure. Warm water is then added until a faint turbidity occurs, and on standing a semi-solid crystalline mass is obtained, which is collected and washed with water. To remove a wax the crystals are digested first with chloroform and then with ether, and the product is purified by repeated crystallisation from pyridine and water. When crystallised in this manner carthamin contains pyridine of crystallisation, which is best removed by drying the substance at 125° or 160°.

Carthamin consists of bright scarlet-coloured prismatic needles which melt and decompose

at about 228°–230°, it is very sparingly soluble in methyl and ethyl alcohol, and is insoluble in ether. It dissolves in cold dilute alkali hydroxides, sodium carbonate, and ammonia with an orange colour, and is reprecipitated by acids unchanged. With sulphuric acid carthamin forms a dull red-coloured solution, which after heating to 100°, gives with water a violet precipitate, possessing feeble mordant dyeing properties, and is soluble in alkalis with a green coloration. Carthamin is decomposed by heating with dilute mineral acids with formation of a dull brown precipitate. The formula of carthamin is, or closely approximates to, $C_{25}H_{24}O_{12}$, and the anhydrous substance is extremely hygroscopic and takes up two molecules of water of crystallisation.

Monopotassium carthamin $C_{25}H_{23}O_{12}K$ is formed when the finely powdered colouring matter suspended in boiling alcohol is treated with strong aqueous potassium acetate solution. It consists of green iridescent needles, and is decomposed by hot water with liberation of the free colouring matter.

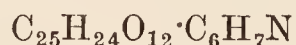
Benzoyl carthamin $C_{25}H_{17}O_{12}(C_7H_5O)_7$ consists of a pale red amorphous powder which melts and decomposes at about 230°–235°. An *acetyl*-derivative has been prepared, the analysis of which agrees fairly well with the formula $C_{25}H_{17}O_{12}(C_2H_3O)_7$.

On account of the extreme sensitiveness of carthamin to alkali (*see later*), it does not appear to be possible to obtain a pure methylation product of this colouring matter by ordinary methods, and the employment also of diazomethane has not given a successful result.

With nitric acid carthamin yields *picric acid*. When fused with alkali *p-hydroxybenzoic acid* and *acetic acids* are formed. By the action of boiling potassium hydroxide solutions varying in strength from 50 to 1 p.c., a brownish-yellow coloured liquid is quickly produced, which on neutralisation gives a brown precipitate, not susceptible to crystallisation. The filtrate from this contains *p-coumaric acid*, and *p-hydroxybenzaldehyde*. No third product soluble in ether could be obtained by this reaction.

When carthamin in 1 p.c. sodium carbonate solution is treated with hydrogen peroxide *p-coumaric acid* is produced, and the crude methylation product of the colouring matter similarly treated gives *p-methoxycinnamic acid*. By oxidation with chromic acid *anisic acid* and *anisic aldehyde* are obtained.

Kametaka and Perkin were unable to prepare the yellow compound which, according to Schlieper (*l.c.*) and Radcliffe (*l.c.*), is produced by boiling carthamin with alcohol, and consider that the pure substance does not give this reaction. By boiling the colouring matter with alcoholic aniline solution, a yellow crystalline substance *aniline xanthocarthaminate*



is readily formed. It consists of needles decomposing at 276°–278°, sparingly soluble in alcohol. In a similar manner *β -naphthylamine xanthocarthaminate* $C_{25}H_{24}O_{12} \cdot C_{10}H_9N$, orange-coloured leaflets, decomposing at about 266°–268°, can be prepared, and the corresponding *ψ -cumidine*-derivative, orange-coloured leaflets, decomposes at about 290°.

These compounds are probably the salts of

an acid which is termed *xanthocarthaminic acid*; it appears to be isomeric with carthamin, and is probably closely related to it. It was observed that when the *β -naphthylamine* compound is dissolved in potassium hydroxide solution, the clear yellow liquid becomes cloudy with separation of *β -naphthylamine*. When this latter is removed, and the alkaline liquid is neutralised with hydrochloric acid, a curdy yellow precipitate slowly separates, and this on standing gradually becomes red coloured, a change which is probably due to the reproduction of carthamin. On account of the large amount of oxygen which carthamin contains it is considered possible that an aliphatic nucleus may be present in this colouring matter.

Previous to the discovery of safranine and of the eosins, safflower was frequently used for the production of brilliant pinks or reds, chiefly on cotton or silk. The mode of dyeing is practically the same as that already given in describing the process of obtaining carthamin. The safflower in bags is well washed with cold water, in order to remove the yellow colouring matter, and the red colouring matter is then extracted by treatment with a cold dilute solution of sodium carbonate. In this solution the material to be dyed is worked about, at the same time adding 'lime juice' (citric acid) gradually until in slight excess. Safflower extract is applied in a similar manner.

Dyers usually gave the washed safflower several successive treatments with alkali, employing at first weak and afterwards strong alkaline solutions. The weak solutions give the brightest and purest tints; hence very delicate colours are dyed with these alone, whilst full colours are first dyed with the inferior extracts, and then 'topped' or 'bloomed' by a dyeing in the purer solutions. The shades obtained from safflower were at one time considered to be the finest and most delicate which a dyer could produce. On the other hand, they were not only expensive but had the disadvantage of being extremely unstable.

Safflower is a very weak dyestuff, for 4 ozs. are necessary to dye 1 lb. of cotton light pink, 8 ozs. for a rose-pink, and about 1 lb. to produce a full crimson.

It is now rarely, if ever, employed in Europe as a dyestuff, but large quantities are still cultivated, more especially in India, and employed for dyeing and pigment manufacture in the East.

Carthamin was sold in a more or less pure condition as a thin aqueous paste, under the name of *Safflower extract* or *Safflower carmine*, but this product is now difficult to obtain in Europe. On the other hand, considerable quantities are still manufactured in Japan, where it is very largely employed as a cosmetic. Carthamin ground up with starch, talc, &c., is used as rouge.

For other references, *v. Dumas*, *Annalen*, 27, 147; *Liebermann*, *Ber.* 7, 247; 8, 1649; *Döbereiner*, *J. Phys. Chem.* 26, 266; *Salvetat*, *Ann. Chim.* [3] 25, 337; *J. pr. Chem.* 44, 475; *Dufour*, *Ann. Chim.* 48, 283. A. G. P.

SAFFLOWER OIL (*Saffron oil*). Safflower oil is obtained from the seeds of *Carthamus tinctorius* (Linn.), a plant until recently cultivated

all over India for the preparation of the saffron dye. The chief localities where the plant is grown are Bengal, Hyderabad, Cawnpore, Bombay, and the Punjab. Two distinct varieties of the plant are grown, *Carthamus tinctorius* (Linn.), and *Carthamus oxyacantha* (Bieb.). The cultivation of the plant has also been extended to Egypt, the Caucasus, and Turkestan. The seeds contain from 23 to 34 p.c. of oil, but owing to the thick husk, only 17 to 18 p.c. of the oil is obtainable by pressing. The press-cake contains, therefore, a large amount of woody fibre as the following analysis of a pressed cake shows:—

	Per cent.
Proteins	20·11
Oil	11·91
Starch, sugar, &c. . .	10·83
Woody fibre	40·75
Moisture	11·60
Ash	4·80

The ordinary Anglo-American rollers have been found unsuitable on account of the extreme hardness of the husk.

The oil is prepared in India on a small scale from two kinds of fruits—the cultivated white and glossy form, and the small fruit of a mottled brown, grey, or white appearance. The oil obtained from the cultivated variety by expression in the cold is pale yellow; it has a pleasant taste, resembles that of sunflower oil, so that it can be used largely for edible purposes. Considerable quantities are pressed in India together with other seeds, especially arachis nuts.

The saturated fatty acids contained in safflower oil consist of palmitic and stearic acids, the unsaturated fatty acids consist of oleic and linolic acids, and small quantities of linolenic acid. Sp.gr. 0·9258 at 15·5°; acid value 9·78; saponification value 197·3; ester value 187·5; Hehner value 95·7; unsaponifiable value 1·25; glycerol 4·26 p.c.

Safflower oil has good drying powers, and although it cannot replace linseed oil in all its applications, it should certainly form a substitute for it in many instances, and find extended use in the manufacture of soft soap. Cf. Mann and Kanitkar (J. Soc. Chem. Ind. 1919, 36 T.); Howard and Remington (*ibid.* 1922, 109 A.).

Safflower oil is heated by the natives to obtain an oil suitable for the preservation of leather vessels, ropes, &c., exposed to the action of water. A specimen of oil thus prepared had the sp.gr. 0·9634, the saponification value 188·0, and the iodine value 128·9. It therefore represents a kind of 'boiled oil.' This 'boiled oil,' termed by the natives 'roghan,' is employed in Lahore, Delhi, Bombay, and Calcutta for the manufacture of 'Afridi wax linoleum.' It is also used by the natives for drawing artistic designs on woven cloth, the production of which was considered for a long time a valuable secret. The pattern is made by means of finely pointed staves dipped in the 'roghan,' which is drawn in very fine threads, and so deposited on the cloth. When completely dry, it forms an indelible pattern.

Considerable quantities of safflower oil are used as a burning oil, notably in Egypt.

J. L.

SAFFRON. Saffron consists of the dried petals of the *Crocus sativus* (Linn.), a plant which flowers in September and October, and is distinct from the ordinary spring crocus (*Crocus vernis*, All.). It is a native of the East, but is cultivated in Spain, the south of France, and Austria, and is employed for flavouring purposes, for the staining of articles of diet, and to a very limited extent as a dyestuff.

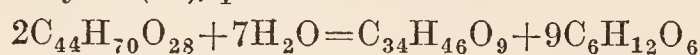
Saffron is sold in two qualities: ordinary saffron (*safran courant*), consisting of the three red stigmata joined to a single yellow style and known in certain pharmacopœias as *Crocus naturalis*; and cut saffron or Austrian saffron, composed of the red stigmata freed from the style and known also as *Crocus electus*. Adulteration of saffron with plant juices, sodium glyceroborate, or potassium nitrate is now rarely encountered, the usual method consisting in steeping saffron for a time in a solution of sugar or sodium sulphate and then allowing it to dry slowly in the air. Genuine saffron imparts to the flame the violet colour due to potassium or, in some cases, an orange, but never a yellow tint. Adulteration with sugar is indicated by an orange-yellow flame which obscures the violet potassium coloration. A suspected sample may be analysed as follows: The saffron is dried at 95°–100°C. for two hours, and after powdering for a further period of an hour, the dried powder is kept in a desiccator over sulphuric acid. Estimations are made, on this material, of: (1) The nitrogen. (2) The ash. (3) Reducing power, before and after inversion by acid. For this purpose 2·5 grms. of the saffron are placed on a glass-wool plug in a tube about 30 mm. in diameter and 15 cms. long, drawn out at one end, about 200 c.c. of water being allowed to fall, drop by drop, on to the saffron; the filtrate is made up to 250 c.c. and filtered, and the two reducing powers measured. (4) Sodium sulphate. This may be detected in the aqueous extract by addition of barium chloride, and may be estimated by evaporating this extract to dryness, incinerating the residue and estimating the sulphate in the ash. The percentage of nitrogen in ordinary saffron is 2·30, and that in cut saffron 2·40, and the difference of the actual amount from these figures serves to calculate the extent of adulteration. With genuine saffron the reducing power towards Fehling solution is slightly increased by inversion with acid, the amount of added sucrose being deduced by multiplying by 0·95 the difference between the reducing powers before and after inversion (G. Pierlot, Ann. Falsificat. 1923, 16, 215; The Analyst, Aug. 1923, 389).

Saffron contains the aromatic oil known as *saffron oil*, *picrocrocin*, a bitter compound, and *crocine*, or *poylchroit*, the glucoside of the colouring matter. Pfyl and Scheitz (Zeit. Nahr. Genussm. 1908, 16, 337) failed, however, to obtain Kayser's 'picrocrocin' (Ber. 17, 2228) though using the methods employed by him. These authors state that by extraction of saffron with chloroform they isolated three products: (i) a colourless crystalline substance, m.p. 280°C., which does not reduce Fehling's solution; (ii) a yellow crystalline substance, m.p. 164°C., readily soluble in water or alcohol, which when boiled with acid developed the odour of saffron oil, and gave a sugar,

probably lævulose; and (iii) a crystalline hydrocarbon, m.p. 118°C. (*cf.* Schüller, Diss. Munich, 1899, and Hilger), apparently similar to the hydrocarbon found in marigold petals, arnica flowers, &c. According to these authors, the second substance referred to above somewhat resembles the 'picrocrocin' described by Kayser. From alcoholic extraction of saffron the same authors obtained (i) the colouring matter; (ii) a sugar (possibly lævulose); and (iii) a glucoside, which on hydrolysis yields saffron oil and a sugar (possibly lævulose).

Crocin $C_{44}H_{70}O_{28}$ (?) forms a yellow-brown amorphous powder, readily soluble in water and dilute alcohol, and dissolves in sulphuric acid with a deep blue coloration which, on standing, becomes violet, then red, and finally brown (*cf.* BIXIN, NYCANTHIN, and CAROTIN).

When digested with hot dilute hydrochloric or sulphuric acids, crocin is hydrolysed into crocetin and glucose, a reaction which, according to Kayser (*l.c.*), proceeds as follows:—



Crocetin consists of a red amorphous powder, readily soluble in alcohol and soluble in alkaline solutions with an orange-red colour. Kayser assigned the formula $C_{34}H_{46}O_9$ to crocetin, but according to Weiss (J. pr. Chem. 101, 65) this is more probably $C_{16}H_{18}O_6$, whilst Schunck and Marchlewski (Annalen, 278, 357) find that Kayser's analytical figures are in agreement with the simpler formula $C_{15}H_{20}O_4$. Decker (Arch. Pharm. 1914, 252, 139) has shown that although crocetin is amorphous it yields crystalline salts with alkalis, and by analysis of these and molecular weight determinations of the acetyl derivative, he concludes that crocetin has the composition $C_{10}H_{14}O_2$.

The sodium or potassium salts are obtained by adding alcoholic sodium, or potassium, hydroxide to a solution of crocetin in dilute aqueous caustic soda, or potash, till no further precipitate is formed, warming, when the respective precipitates redissolve, and then allowing the solution to cool when the salts separate in a crystalline condition. *Crocetin sodium salt* crystallises in needles; the *potassium salt* in nodular aggregates; the *ammonium salt*, from dilute alcohol, in lustrous red needles. Other salts—aniline, pyridine and quinoline—have also been prepared by Decker.

Acetylcrocetin $C_{10}H_{13}O_2(CH_3CO)$ crystallises in red needles, m.p. 174°C. It is prepared by heating the potassium salt with acetyl chloride. With lead acetate crocetin gives a deep brown precipitate, and with sulphuric acid a deep blue solution.

When crocetin is brominated in chloroform solution, a *dibromide* is produced which crystallises in yellow octahedra, m.p. 103°–104°C., and the production of this is considered by Decker as evidence of the presence of a double bond in the crocetin molecule.

When oxidised with bromine in alkaline solution, crocetin yields a product $C_7H_{10}O_2Br_2$, which forms colourless felted needles.

Dyeing properties.—Crocetin dyes aluminium and tin mordanted fabrics dull orange and yellow shades respectively.

According to Rochleder, the Chinese dyestuff 'Wongsky' (*q.v.*), which consists of the fruit

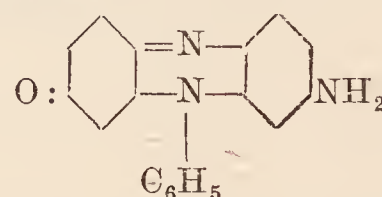
of the *Gardenia grandiflora* (Lour.), also contains crocin (Jour. Chem. Soc. 1858, 475). A. G. P.

SAFFRON OIL *v.* SAFFLOWER OIL.

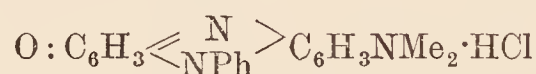
SAFFRON SURROGATE *v.* VICTORIA YELLOW.

SAFRANINES and *apo*-SAFRANINES *v.* AZINES AND COLOURING MATTERS DERIVED FROM THEM.

SAFRANINONES. *Safraninone*,

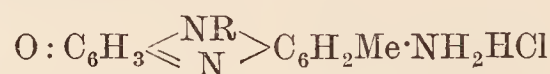


(*Aminobenzolindone*) may be prepared by oxidising a mixture in molecular proportions of *p*-phenylene-diamine and *m*-hydroxy-diphenylamine with potassium dichromate (Jaubert, Ber. 1895, 28, 270); by heating phenosafranine hydrochloride with aqueous sodium acetate at 150° (Fischer and Hepp, Ber. 1897, 30, 399); by heating safraninone with ammonia at 180°, and in other ways (Jaubert, *l.c.*). It forms prisms with bluish-green lustre, readily soluble in water with a red colour and brownish-yellow fluorescence. When heated with ammonia at 180° it forms a little phenosafranine, and when boiled with alkalis it yields safraninone and ammonia. Safraninone forms a blue diazo-compound, which condenses with β -naphthol giving a blue colouring matter. The *acetyl* derivative of safraninone forms fine, red needles, with copper-like lustre, and melting above 280°. Safraninone also condenses with aldehyde, and when heated with sulphur and alkali sulphides it forms a violet cotton dye (D. R. P. 126175; Chem. Zentr. 1901, ii. 1108). The hydrochloride of the *dimethyl derivative*



is a brownish crystalline powder, readily soluble in water (Jaubert, *l.c.*).

Safraninones containing aliphatic groups are very readily prepared by the further oxidation of the indophenols obtained either by condensing the nitrosophenols with the 4-alkyltolylene-2 : 4-diamines, or by oxidising a mixture of these bases with the *p*-aminophenols. A number of these safraninones



have been described (D. R. P. 189078).

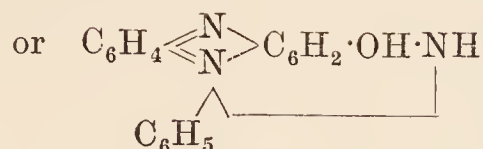
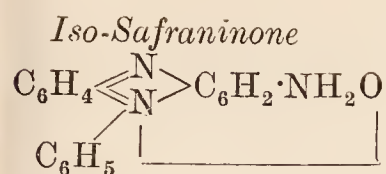
They form valuable substances for the preparation of red sulphur dyes.

The product of reaction of molecular proportions of an aldehyde bisulphite and *m*-tolylenediamine is mixed with an alkaline solution of nitrosophenol, and after making slightly acid and stirring for a few hours, the mixture is made slightly alkaline and oxidised with manganese dioxide. When formaldehyde bisulphite is used the safraninone



is formed.

Sulphide dyestuffs which dye cotton reddish shades are obtained by heating these safraninones with sodium sulphide and sulphur, with or without addition of metallic salts (Eng. Pat. 24008, 1906).



is obtained by the action of sulphuric acid on pheno-*iso*-safraninone.

The violet-brown glistening needles of the *iso*-safraninone chloride obtained on adding sodium chloride are purified and their aqueous solution is treated with ammonia or ammonium carbonate when the *iso*-safraninone separates as blackish-brown needles, m.p. 310°–315° (decomp.) readily soluble in hot water and in alcohol with a green colour (Kehrmann and Kramer, Ber. 1900, 33, 3074).

SAFRANISOL, SAFRANOLS *v.* AZINES.

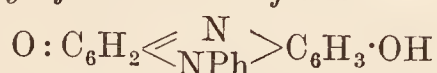
SAFRANONE (*Benzolindone, Aposafrazone*)

$\text{O} : \text{C}_6\text{H}_3 \begin{array}{c} \text{N} \\ \diagup \quad \diagdown \\ \text{NPh} \end{array} \text{C}_6\text{H}_4$ is prepared by treating the ferric chloride double salt of phenylphenazonium chloride with excess of sodium hydroxide (Kehrmann and Schaposchnikoff, Ber. 1897, 30, 2623). It may also be obtained by treating anilinoaposafranine with barium hydroxide at 140° (Fischer and Hepp, Annalen, 1895, 287, 193), or aposafranine hydrochloride with sodium hydroxide (Kehrmann, Ber. 1895, 28, 1716); by removing the amino- group from safraninone or by heating azo-safraninone with 75 p.c. sulphuric acid (Jaubert, Ber. 1895, 28, 275), and by other methods (Kehrmann and Burgin, *ibid.* 1896, 29, 1819).

Safranone forms small brown needles with a green metallic lustre, m.p. 248°–249°, and dissolves with a magenta colour in water, and with a green colour in sulphuric acid, which turns to rose colour on dilution.

When treated with phosphorus oxychloride it yields chlorophenylphenazonium chloride (Fischer and Hepp, Ber. 1897, 30, 1827; *ibid.* 1898, 31, 299). According to Fischer and Römer (*ibid.* 1907, 40, 3406) the amino- group may be introduced by means of hydroxylamine only into such safranones as have both the ortho-positions with respect to the oxygen atom, free.

Hydroxysafranone or safranol



may be prepared by heating an aqueous solution of nitrosophenol with *meta*-hydroxydiphenylamine and sodium hydroxide (Hewitt, Newman and Winmill, Chem. Soc. Trans. 1909, 580), or by oxidising a mixture of *p*-amino-phenol and *meta*-hydroxyphenylamine in presence of mineral acid (Jaubert, *l.c.*), and by other methods (Fischer and Hepp, Ber. 1895, 28, 2283; *ibid.* 1896, 29, 361; *ibid.* 1905, 38, 3435). It is a crystalline substance, m.p. above 330°, almost insoluble in most ordinary solvents, but readily soluble in alkalis.

The *ethyl* (m.p. 265° decomp.) and *methyl* ethers (m.p. 240°) (Fischer and Hepp, Annalen, 1895, 286, 212), the *acetyl* (m.p. 271°) (Hewitt, *l.c.*), the *sulphonic acid*, and *naphtho-* derivatives (Jaubert, Ber. 1898, 31, 1185), have been prepared. When heated with sulphur and an alkali sulphide, safranol forms a bluish-violet cotton

dye (D. R. P. 126175; Chem. Zentr. 1901, ii. 1107).

Halogen (Fischer and Hepp, Ber. 1900, 33, 1485) and other derivatives of safranone have been prepared (Kehrmann, *ibid.* 1895, 28, 1712; Fischer and Hepp, *ibid.* 2287; Kehrmann and Fühner, Annalen, 1896, 290, 301; Kehrmann and Duret, Ber. 1898, 31, 2437; Fischer and Hepp, Chem. Zentr. 1902, ii. 903; Kehrmann and Masslenikoff, Ber. 1912, 45, 2891).

SAFROLE (*safrol, shikimole*) $\text{C}_{10}\text{H}_{10}\text{O}_2$ (St. Evre, Ann. Chim. Phys. [iii.] 12, 107; Grimaux and Knotte, Compt. rend. 68, 928) is contained in camphor oil, a waste product of camphor distillation, and gives to it its characteristic odour (Chemist & Druggist, 40, 592). Safrole is the essential constituent of oil of sassafras (from *Sassafras officinale* (Nees) [*Laurus Sassafras* (Linn.)]), of which it forms 78 p.c. (Power and Kleber, Pharm. Review, 1896); it also occurs in many other plants of the order *Lauraceae*, in the essential oil of *Illicium religiosum* (Sieb. et Zucc.) (Flückiger, J. Pharm. Chim. [iii.] 17, 989; Eijkman, Rec. trav. chim. 4, 32), in massoybark oil (Wey, Arch. Pharm. [iii.] 28, 22), and in oil of *Cinnamomum zeylanicum* (Nees) (Duyk, J. Pharm. d'Anvers, 1896, April; see also Goulding, Chem. Soc. Trans. 1903, 1099).

The leaves of *Doryphora sassafras*, the New South Wales variety of the sassafras tree, yield from 0.1 to 1.05 p.c. of essential oil according to season. Leaves from the Monga district give an oil having sp.gr. 1.01–1.02 $n_D^{20} = 1.506$ –1.509, ester value 4.6, ester value after acetylation 32.97, solubility in 70 p.c. alcohol 1 in 8 contains safrole 60–65 p.c., camphor 10–15 p.c., *d*- α -pinene 10 p.c., sesquiterpenes 10 p.c., eugenol 1 p.c. Leaves from the Currowan district give an oil lighter than water (sp.gr. 0.9808) and only contain about 30 p.c. of safrole, and considerable quantities of eugenol methyl ether, and about 30 p.c. of camphor (Penfold, Perf. Essenl. Oil. Rec. 1922, 13, 273).

Safrole is obtained from 'red-oil' (a product of fractionating camphor oil, containing 20 p.c. of safrole), or from oil of sassafras, by freezing it out; and is purified by recrystallisation.

At ordinary temperatures it is a clear, colourless oil, having an odour of sassafras and a sharp taste. Cooled to -20° it solidifies in rhombic prisms (ratio of axes; $a : b : c = 0.31658 : 1 : 0.57832$, $\beta = 111^\circ 59' 5$, Arzruni, N. Rep. Pharm. 25, 615); m.p. 12° (Sugiyama, J. Soc. Chem. Ind. 1902, 1551), 8.5° – 10° (Arzruni), 8° (Schiff, Ber. 17, 1935); b.p. 230° – 235° (Sugiyama), 232° (Schiff); sp.gr. 1.107 at 15° ; impure commercial safrole has sp.gr. 1.1040–1.1065 (Sugiyama).

Safrole is used in soaps to cover the odour of the fatty basis, and has been introduced into America, under the name *safrine*, as an artificial oil of sassafras.

Safrole $\text{CH}_2\text{O}_2 : \text{C}_6\text{H}_3 : \text{C}_3\text{H}_5$ can exist in five isomeric forms, all of which are known; the commercial product is a mixture of two or more of these.

Safrole, the *methylene ether* of *allyldihydroxy-benzene* (Poleck, Ber. 1889, 22, 2861), has the formula

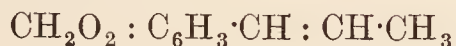


on the preceding compound. It has m.p. 72° ; the *monohydrochloride* has m.p. 246° with decomposition; *benzoyl derivative* melts at 248° .

Nitroaminodihydrosafrole ($\text{NH}_2 : \text{NO}_2 = 2 : 6$), prepared by the action of ammonium sulphide on the dinitro-compound, melts at 76.5° (Thoms and Blitz).

For other derivatives see Foulds and Robinson (*l.c.*).

iso-Safrole (isafrole)



is the *methylene ether* of *propenyldihydroxybenzene* (Balbiano and Paolini, Ber. 1902, 35, 2994). It is obtained: (1) by heating safrole with alcoholic KOH (Ciamician and Silber, Ber. 1890, 23, 1159); (2) by heating safrole to 200° with dry NaOEt (Angeli, Gazz. chim. ital. 1893, 23, ii. 101); (3) by heating safrole with a solution of sodium amyloxide in amyl alcohol at 260° (Gassmann, Compt. rend. 1897, 124, 38).

That *iso-safrole* has the above constitution is shown (1) by its production on heating methylenebromocaffeic acid (Moureu, Compt. rend. 1896, 122, 792); (2) by its production from β -piperonyl- α -methyl-acrylic acid by loss of CO_2 (Wallach, Annalen, 1907, 357, 72); (3) by its behaviour on oxidation. Mercuric acetate oxidises it to the *glycol*, $\text{CH}_2\text{O}_2 : \text{C}_6\text{H}_3 \cdot \text{C}_3\text{H}_5(\text{OH})_2$, m.p. 101° – 102° (Balbiano and Paolini, Ber. 1903, 36, 3575); it is oxidised by ozone to piperonal (Otto, Ann. Chim. Phys. 1898, [viii.] 13, 77; Nagai, J. Chem. Ind. Japan, 1922, 25, 631).

iso-Safrole exists in two stereoisomeric forms which can be partially separated by fractional distillation.

α -*isoSafrole* is obtained by steam distillation of the first fractions, from which the safrole has been removed by mercuric acetate. The β -*iso-safrole* is fixed as the picrate and does not come over.

The α - compound has b.p. 116.2° – 116.3° at 13.5 mm., 242.2° – 242.5° at 760 mm., sp.gr. 1.1073 at 18.5° , n_D 1.5678 at 18° (Hoering and Baum, Ber. 1909, 42, 3076).

By gentle isomerisation by dilute alcoholic potassium hydroxide at 82° – 86° an unstable *cis-iso-safrole* is formed, readily changed by alkali at a higher temperature into the *trans-modification* (Nagai, J. Coll. Eng. Tokyo, 1921, ii. 83).

β -*isoSafrole* is the chief constituent of commercial *iso-safrole* and is most easily isolated as the picrate, m.p. 74° (*cf.* Bruni and Tornani, Atti R. Accad. Lincei, 1904, [v.] 13, ii. 184). This, when decomposed by alcoholic NH_3 , yields β -*iso-safrole* as an oil, b.p. 123° at 11.5 mm., sp.gr. 1.1227 at 21° / 17.5° , n_D 1.5786 at 18° .

Both isomerides yield the same glycol and the same dibromide (Hoering and Baum, *l.c.*), and by oxidation with potassium bichromate or with ozone give practically identical yields of piperonal (Nagai, *l.c.*). By boiling *iso-safrole* with a mixture of PCl_3 and PCl_5 *di-iso-safrole* is obtained (Angeli and Mola, Chem. Soc. Abstr. 1895, i. 24).

If an absolute ethereal solution of *iso-safrole* and ferric chloride is treated with dry hydrogen chloride for some days a polymeride of *iso-safrole* is produced, spherical nodules, m.p. 92° (Puxeddu, Gazz. chim. ital. 1913, 43, i.

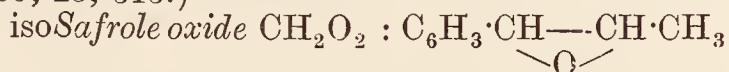
128; 1916, 46, ii. 169; Mayer, Atti R. Accad. Lincei, 1914, [v.] 23, i. 358).

By heating *iso-safrole* hydrochloride with CH_3ONa , $\text{C}_2\text{H}_5\text{ONa}$, or $\text{C}_5\text{H}_{11}\text{ONa}$ the following derivatives are obtained:—

Methoxy derivative, b.p. 110° – 112° at 5 mm.; sp.gr. 1.1116 at 15° ; n_D 1.51619 at 15° ;

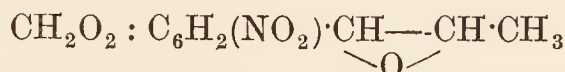
Ethoxy derivative, b.p. 110° – 111° at 3.5 mm.; sp.gr. 1.0796 at 15° ; n_D 1.50884 at 15° .

Amyloxy derivative, b.p. 136° – 137° at 13.5 mm.; sp.gr. 1.0258 at 15° ; n_D 1.49775 at 15° (Schimmel & Co., Chem. Soc. Abstr. 1905, i. 537). (For methods of distinguishing between safrole and *iso-safrole*, see Chapman, Analyst, 1900, 25, 313.)



is formed by the oxidation of *iso-safrole* with iodine and mercuric oxide in alcohol (Bougault, Compt. rend. 1900, 130, 1766; Bull. Soc. chim. 1901, [iii.] 25, 444). It is a liquid, b.p. 140° – 142° at 9 mm. (Hoering, Ber. 1905, 38, 2296); sp.gr. 1.2128 at 17° (Ber. 1905, 38, 3477; D. R. P. 174496).

Nitro-isoSafrole oxide



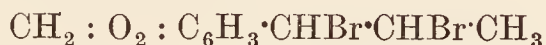
obtained by hydrolysis of β -bromonitro-*acetoxydihydro-iso-safrole* (*v. infra*), has m.p. 113° – 114° .

Bromo-isoSafrole oxide, b.p. 169° – 173° , at 11 mm.; and

Dibromo-isoSafrole oxide, m.p. 134° – 135° , are prepared in an analogous manner.

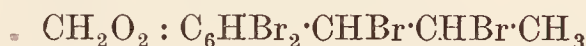
When these oxides are distilled at the ordinary pressure or warmed with dilute acid they are converted into the isomeric *ketones*: $\text{CH}_2\text{O}_2 : \text{C}_6\text{H}_3 \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{CH}_3$, b.p. 283° – 284° , sp.gr. 1.2017 at 17° ; $\text{CH}_2\text{O}_2 : \text{C}_6\text{H}_2\text{Br} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{CH}_3$, m.p. 103° ; $\text{CH}_2\text{O}_2 : \text{C}_6\text{HBr}_2 \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{CH}_3$, m.p. 116° – 117° (Hoering, *l.c.*).

isoSafrole dibromide



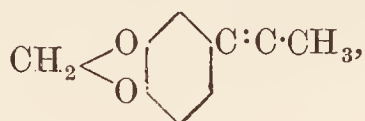
is obtained by the action of bromine water on *iso-safrole*, or by treating safrole with bromine in presence of carbon disulphide (Foulds and Robinson). Forms *bromo-isoSafrole* with loss of hydrobromic acid when distilled under reduced pressure. Warmed with granulated marble in moist acetone it yields the *hydroxy bromide* $\text{CH}_2\text{O}_2 : \text{C}_6\text{H}_3 \cdot \text{CH}(\text{OH}) \cdot \text{CHBr} \cdot \text{CH}_3$, which with alcoholic KOH gives the *oxide* (Hoering, D. R. P. 174496).

Dibromo-isoSafrole dibromide



is prepared by dropping *iso-safrole* quickly into bromine. It is reduced by zinc-dust to *dibromo-isoSafrole*, crystallising in needles, m.p. 149° – 150° .

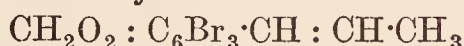
Similarly *bromo-isoSafrole*, m.p. 30° – 33° , b.p. 165° – 170° at 16 mm., can be obtained from *bromo-isoSafrole dibromide*. When heated with methyl alcohol and potassium hydroxide at 125° the former compound yields *piperonylallylene*



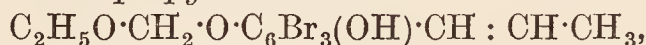
colourless prisms, m.p. 42°–43° (Foulds and Robinson, *l.c.*).

Tribromo-isosafrole- $\alpha\beta$ -dibromide (*iso-safrole pentabromide*) $\text{CH}_2\text{O}_2 : \text{C}_6\text{Br}_3 \cdot \text{CHBr} \cdot \text{CHBr} \cdot \text{CH}_3$ obtained by dropping *isosafrole* into excess of bromine, crystallises in clusters of colourless crystals, m.p. 196.5°–197°.

Tribromo-isosafrole



is produced by reducing the preceding compound with zinc-dust in alcohol; m.p. 110°–111°. Reduced with HI it yields *tribromodihydro-iso-safrole*. Heated with alcoholic KOH at 145°–150° for 5–6 hours it gives the *ethoxymethyl ether* of *tribromopropylencatechol*



m.p. 96°–99° (Hoering, Ber. 1907, 40, 1096).

β -Bromonitro- α -acetoxydihydro-iso-safrole is obtained by the action of nitric acid on *iso-safrole dibromide* in alcoholic solution, in yellow prismatic needles, m.p. 113° (Hoering, Ber. 1905, 38, 3458). *β -Bromonitro- α -methoxydihydro-iso-safrole* is similarly obtained as an oil, b.p. 166°–169° at 11 mm., and 158°–164° at 8 mm. (Hoering, *ibid.* 1905, 38, 3464).

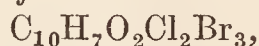
Methoxydibromo-iso-safrole



is produced by the action of MeOH on bromo-*iso-safrole dibromide*; forms needles or prisms, m.p. 75°–76°. The corresponding *ethyl compound* forms large rhombohedra, m.p. 58°–60° (Pond, Erb and Ford, J. Amer. Chem. Soc. 1902, 24, 327; see also Pond and Siegfried, *ibid.* 1903, 25, 262).

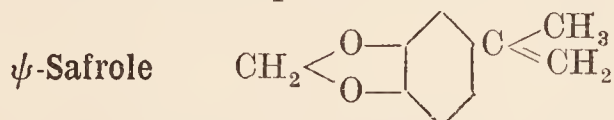
Dibromo-iso-safrole dichloride $\text{C}_{10}\text{H}_8\text{O}_2\text{Cl}_2\text{Br}_2$, m.p. 97°–99°.

Tribromo-iso-safrole dichloride

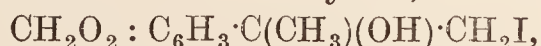


m.p. 173.5°–174.5° (Hoering and Baum, Ber. 1908, 41, 1914).

isoSafrole nitrosite $\text{C}_{10}\text{H}_{10}\text{N}_2\text{O}_5$, produced by the action of nitrous acid on *isosafrole*, forms colourless needles, m.p. 132° (Angeli, Ber. 1891, 24, 3994); m.p. 128° (Wallach, and Müller, Annalen, 1904, 332, 305). Warmed with acetyl chloride, sodium methoxide, or alcoholic KOH it yields *β -nitro-iso-safrole* $\text{CH}_2\text{O}_2 : \text{C}_6\text{H}_3 \cdot \text{CH} : \text{C}(\text{NO}_2) \cdot \text{CH}_3$ in yellow needles, m.p. 98° (W. and M.; cf. Angeli and Rimini, Gazz. chim. ital. 1896, 26, i. 7). Treated with hydroxylamine hydrochloride and sodium carbonate in alcohol it yields *piperonaldoxime*, m.p. 111°.



(1- ψ -allyl-3 : 4-catechol methylene ether) is obtained by the action of magnesium methyl iodide on methyl piperonylate as a colourless liquid, sp.gr. 1.1338 at 0°; 1.1198 at 15°; b.p. 135° at 20 mm., 233°–239° at 760 mm.; n_D 1.5619 at 15°. On reduction it yields 1-isopropyl-3 : 4-catechol methylene ether, and on oxidation piperonyl-acetone. It forms an iodohydrin,



which, when treated with KOH, forms an *ethylene oxide*, b.p. 150°–155° at 15 mm. (Béhal and Tiffeneau, Bull. Soc. chim. 1908, [iv.] 3, 729).

ψ -Safrolechlorhydrin



prepared by the action of moist chlorine on ψ -safrole, is a yellow-coloured oil. By treatment with PCl_5 and subsequent hydrolysis it is converted into *dihydroxyphenyl- ψ -allyl chlorohydrin* $\text{C}_6\text{H}_3(\text{OH}) \cdot \text{CMe}(\text{OH}) \cdot \text{CH}_2\text{Cl}$, a thin oil from which *α -methyl adrenalin* is obtained as a bright golden-yellow powder (Böttcher, Ber. 1909, 42, 253).

SAFROSINE *v.* *Phthaleins*, art. TRIPHENYL-METHANE COLOURING MATTERS.

SAGAPENUM *v.* GUM RESINS.

SAGE CAMPHOR *v.* CAMPHORS.

SAGE OIL *v.* OILS, ESSENTIAL.

SAGO. A product consisting mainly of starch, prepared from the pith of certain palms. *Metroxylon laeve* (Mart.), *M. Rumphii* (Mart.), and *Raphia pedunculata* (Beav.) or *Metroxylon Sagu* (Rottb.) yield the true sago, though the name is given to products derived from other palms, e.g. the Indian palm, *Caryota urens* (Linn.). Large quantities of sago are obtained from the Malacca and Philippine Islands and New Guinea. The sago palms grow best in boggy soils, rich in humus, and each tree yields about 600 lbs. of starch (Dubose, Dingl. poly. J. 1892, 285, 213).

The palms are cut down when the trunks have attained a height of about 20 ft. and a diameter of 20 ins., and the sap allowed to drain away; they are sawn into lengths of 6–8 ft., split open, and the pith, consisting of starch granules intermixed with fibrous matter, removed. This is then pounded in wooden mortars and agitated with water. The milky liquid is then run through sieves to remove fibre and cellular matter and allowed to settle. The sediment is repeatedly washed with water, drained and dried. It constitutes sago flour, and is exported to Europe in that form, for the manufacture of glucose and for use in the textile industries.

A sample examined by Balland (J. Pharm. Chim. 1903, 17, 476) gave the following analytical figures:—

Water	Protein	Fat	Starch	Crude fibre	Ash
12.1	2.1	0.2	80.4	4.0	1.2

Samples of sago flour, as imported into England, were examined by Smetham (J. Roy. Lancashire Agric. Soc. 1909), who found—

	Pro-	Sol. carbo-	Crude		
	Water	tein	Fat	hydrates	fibre
Sago flour . . .	16.8	0.25	0.23	82.3	0.13
„ „ (seconds)	16.3	1.12	0.17	76.9	3.30
					3.80

Granulated sago or pearl sago—the form in which sago is chiefly used as a food—is prepared from sago flour by mixing it with water to form a stiff paste, which is forced through a metal sieve into a heated shallow metal dish which has been slightly greased. The fragments are kept stirred by means of an iron rod and agglutinate into small spherical masses which are usually sorted into sizes and sold in two or three forms, ‘bullet sago,’ ‘pearl sago,’ &c.

Singapore is the chief seat of the sago industry; in 1892 its production amounted to 20,000,000 kilos. (Dubose, *l.c.*).

Sago starch consists mainly of oval or rounded granules, some of which are compound, consisting of one large granule with 1, 2, or 3 smaller ones attached. The large granules are

50–60 μ in length, the smallest ones 10–20 μ . There is a distinct, lineal, transverse, or oblique hilum and distinct striations: often vegetable tissue, cells, and hairs, due to imperfect washing in preparation, are also present.

Pearl sago, under the microscope, shows starch granules in various stages of transformation, some retaining their original shape, others in which the starch has been more or less gelatinised, whilst some are swollen into irregular shapeless masses.

When heated with water, pearl sago does not fall to pieces, but the spherical masses swell up and become gelatinous and almost transparent.

Pearl sago usually contains 12–15 p.c. of water and a small quantity (about 0.15 p.c.) of inorganic matter, the rest being almost all starch, with, doubtless, small quantities of dextrin.

Imitations of pearl sago, prepared from potato starch, have been produced in France and Germany, in some cases, coloration by oxide of iron being adopted (Wittstein, Dingl. poly. J. 1878, 227, 93).

H. I.

SAGROTAN, *p*-chloro-*m*-cresol.

SAINFOIN, *Onobrychis viciaefolia* (Scop.) [= *O. sativa* (Lam.)]. A deep-rooted, perennial, leguminous plant grown for pasturage and hay. It prefers light, calcareous soils, and should be cut early, as after flowering its stems become woody. It yields a vigorous after-growth.

The following analyses are from Kellner:—

	Water	Protein	Fat	N-free extract	Fibre	Ash	Digest. proteids
Beginning to flower	81.0	3.6	0.6	7.9	5.5	1.4	1.9
In full flower	80.0	3.5	0.6	7.8	6.9	1.2	1.6
Hay, cut before flowering	15.8	15.4	3.2	34.0	24.9	6.7	7.8
Hay, cut in flower	16.5	13.2	2.5	32.5	28.0	7.3	7.5

The ash, like that of other *Leguminosæ*, is rich in lime; according to Wolff's analyses, it contains—

K ₂ O	Na ₂ O	MgO	CaO	P ₂ O ₅	SO ₃	SiO ₂	Cl
39.4	1.7	5.8	32.2	10.4	3.3	4.0	3.0

H. I.

SAIODIN *v.* SYNTHETIC DRUGS.

SAKÉ. A very popular drink in Japan. It is prepared from rice by fermentation, the manufacture being carried on from September to February only, as in the summer the fermentation cannot be properly controlled. It is a light-yellow liquid, having a peculiar flavour somewhat resembling a mixture of beer and sherry. Its sp.gr. is about 0.99, and it contains on an average 17 p.c. of alcohol by volume, or nearly 30 p.c. of proof spirit.

The manufacture is described by M. Ikuta (Zeitsch. anal. Chem. 14, 439) as follows:—

1. *Preparation of koji*. The finest rice is boiled in an iron kettle with sufficient water to soften it. After cooling, it is brought into the koji chamber, the outside walls of which are covered with earth and the interior with straw, by which means the temperature of the interior is kept up.

The rice is here mixed with a little *moyaschi* (a yeast obtained from a previous fermentation) and remains in the chamber for two days, by which time most of the starch of the rice is

converted into dextrose, and it is then called *koji*.

2. *Preparation of motoh*. *Koji*, fresh-boiled rice, and water are mixed in a wooden vat in the proportion to form a thin paste. Wooden casks containing warm water are placed in this liquid every day. After one or two days a frothy fermentation takes place, which is allowed to continue 30–40 days, during which time the temperature rises to 37°. At the end of the period the liquid contains 10 p.c. of alcohol, and is called *motoh*.

3. *The third stage*. Freshly boiled rice, *koji* and *motoh* are mixed with a little water. The mixture ferments a little, but without appreciable rise in temperature. As soon as the froth ceases to form on the surface, *i.e.* in 8–10 days, the process is finished. The fermented fluid is filtered through cotton bags and put into casks, and allowed to stand until clear. It is heated in an iron vessel to 44°, and is then run into casks.

The residue remaining in the cotton sacks has been used from time immemorial in Japan for the manufacture of vinegar.

The preparation of saké is accelerated, and a more uniform product obtained by steaming the rice, previously soaked in water, then spreading on mats and sprinkling with *Aspergillus oryzae*. The mats are kept in the dark, and the mass, when covered with mould, is thoroughly mixed about twice every 24 hours for 3 or 4 days. The *koji* thus prepared is sometimes dried and preserved in this form for future use.

A fermented liquor is then prepared from a mixture of *koji*, water, and steamed rice, and this in its turn is used for fermenting about seven times its weight of a mixture of boiled rice and water in nearly equal proportions, the whole process requiring about 30 days.

Saké is usually taken hot by the Japanese immediately before meals. It has intoxicating effects of a speedy but transient character.

A somewhat similar beverage is made from rice in Java and Borneo (*see also* ARRACK).

J. C.

SAKOA OIL. A non-drying oil extracted from the seeds of *Sclerocarpa caffra*, growing in Madagascar and locally known as sakoa. The seeds contain 56 p.c. of the oil, which has the following characteristics: d^{15} 0.9167; n^{40} 1.460, saponification number 193.5; iodine number 76.6; Reichert-Meissl number 0.1; Polenske number 0.45; unsaponifiable matter 0.6 p.c.; m.p. of fatty acids 25° (Jumelle, Mat. Grasses, 1921, 13, 5854).

SAKURANIN *v.* GLUCOSIDES.

SAL ABSINTHII. Salt of wormwood. Impure potassium carbonate made from the ashes of the plant.

SAL ACETOSELLÆ. *Acid potassium oxalate v. OXALIC ACID*.

SAL ALKALI MINERALE. *Sodium carbonate*.

SAL ALKALI VEGETABILE. *Potassium carbonate*.

SAL ALKALI VOLATILE SICCUM or **SAL VOLATILE**. *Ammonium sesquicarbonate*.

SAL AMARUM. *Magnesium sulphate*.

SAL-AMMONIAC (*Salmiac*, Fr.; *Salmiak*, Ger.). Ammonium chloride, NH₄Cl, crystallised

in the cubic system with plagihedral-hemihedrism as in sylvite; sp.gr. 1.532. In nature it occurs mainly as a volcanic sublimation, either around fumaroles or filling cavities in the lava. After certain eruptions of Vesuvius and Etna a few hundredweights of the salt have been collected for local use. Other volcanoes that have yielded sal-ammoniac are those of the Lipari Islands, Mt. Hecla in Iceland, Kilauea in Hawaii, Martinique, &c. The little-known volcanoes of Central Asia are also often mentioned, whence the salt was taken into China and to the West through Armenia under the name *salarmoniac*.¹ It is also formed by the burning of coal seams, some of the best crystallised specimens being of this origin, e.g. from Burgk and Zwickau in Saxony, and St. Etienne in France. It has further been detected in guano deposits. L. J. S.

SAL APERITIVUM FRIEDERICIANUM. *Sodium sulphate.*

SAL AURI PHILOSOPHICUM. *Acid potassium sulphate.*

SAL CATHARTICUM. *Magnesium sulphate.*

SAL CORNU CERVI. *Ammonium carbonate.*

SAL DE DUOBUS or **SAL DUPLICATUM.** *Normal potassium sulphate.*

SAL DIGESTIVUM SYLVII or **SAL FEBRIFUGUM SYLVII.** *Potassium chloride.*

SAL FUSIBILE. *Sodium ammonium phosphate.*

SAL MARINE. Common salt or Sodium chloride.

SAL MARTIS. Green vitriol or Ferrous sulphate.

SAL MICROCOSMICUM. *Sodium ammonium phosphate.*

SAL MIRABILE. *Sodium sulphate.*

SAL MIRABILE PERLATUM. *Disodium orthophosphate.*

SAL NARCOTICUM VITRIOLI. *Boric acid.*

SAL NATIVUM. *Sodium ammonium phosphate.*

SAL POLYCHRESTUM GLASERI, S. LAMERIANUM, S. PARISIENSE. *Normal potassium sulphate.*

SAL POLYCHRESTUM SEIGNETTI. *Rochelle salt; Sodium potassium tartrate.*

SAL PRUNELLA. Fused nitre cast into sticks or balls.

SAL SATURNI. *Lead acetate.*

SAL SECRETUM GLAUBERI. *Ammonium sulphate.*

SAL SEDATIVUM HOMBERGII. *Boric acid.*

SAL SUCCINI. *Amber.*

SAL TARTARI. *Potassium carbonate.*

SALACETIN (*Saletin*). Trade names for acetyl-salicylic acid.

SALACETOL v. SALICYLIC ACID and SYNTHETIC DRUGS.

SALAERATUS. A term applied in the United States to a baking powder consisting of a mixture of sodium carbonate, salt, and cream of tartar or tartaric acid.

SALANTOL v. SALICYLIC ACID.

SALARGYL. A combination of silver oxide and proteoses.

SALENIXON. Crude potassium sulphate, as obtained in the manufacture of nitric acid.

SALEP v. GUMS.

¹ The *Ammoniacum* of Pliny was a tree gum, and his *Sal ammoniacus* was, perhaps, sodium chloride.

SALHYPNONE v. SALICYLIC ACID.

SALIBROMIN, SALIMENTHOL, and SALIPYRIN v. SYNTHETIC DRUGS.

Constitution of Salipyrine.—Although salipyrine is usually represented as antipyrine salicylate, it may possibly be an additive compound, e.g. $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{O}\dots\text{H}\dots\text{C}_{11}\text{H}_{12}\text{ON}_2$. Antipyrine is a very weak base ($k=2.8\times 10^{-13}$), its salts in dilute solution being considerably hydrolysed. Aqueous or alcoholic solutions of salipyrine show only the reactions of its components. The alteration of E.M.F. produced by the addition of salipyrine to a cell containing a suspension of silver salicylate in saturated salicylic acid against a standard calomel electrode has been determined in comparison with the effect produced by the addition of such acids and bases, and from the results it is concluded that undissociated salipyrine consists of an additive complex corresponding with the above formula. The conductivity of solutions of antipyrine hydrochloride has been studied and additive compounds of antipyrine with the following phenols have been obtained: vanillin, *p*-cresol, nitroresorcinol, protocatechualdehyde, and *p*-hydroxybenzaldehyde (S. Bodforss and A. Guthe, Ber. 1924, 57 [B], 842-846; Chem. Soc. Abstr. 1994, 126, i. 770).

SALICIN v. GLUCOSIDES.

SALICREOL (*Salocreol*). Creosote salicylate.

SALICYL ALCOHOL. *Saligenin; Saligenol o-hydroxybenzyl alcohol; 1:2-phenol-methylol* $\text{C}_6\text{H}_4(\text{OH})\cdot\text{CH}_2\cdot\text{OH}$. Obtained by the reduction of salicylaldehyde (*q.v.*), and by the hydrolysis, by means of emulsin and salicase, of salicin (*q.v.* art. Glucosides); by heating phenol with methylene chloride and aqueous sodium hydroxide at 100°. Crystallises in white tables or rhombohedral plates, m.p. 82°. Readily soluble in water, alcohol, ether, or chloroform. Gives a blue colour with ferric chloride. With sulphuric acid forms *saliretin* $\text{C}_{14}\text{H}_{14}\text{O}_3$, a yellowish powder, insoluble in water. Heated with glycerol at 100° yields *saliretone* $\text{C}_{14}\text{H}_{12}\text{O}_3$, a crystalline powder, m.p. 121.5°.

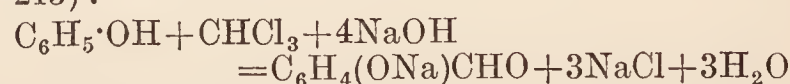
Salicyl alcohol (saligenin) finds application as a remedy for rheumatism, and as a local anæsthetic with an action similar to that of novocaine. Has been introduced into commerce for anæsthetic purposes under the name of *salicaine*.

For derivatives of saligenin of pharmacological interest, see Hart and Hirschfelder (J. Amer. Chem. Soc. 1921, 43, 1688).

SALICYLALDEHYDE ('*salicylide*')

$\text{C}_6\text{H}_4(\text{OH})\text{CHO}$ (1, 2).

Occurs in the oil from *Spiræa Ulmaria* (Linn.) and other species of *Spiræa*. Obtained, along with the isomeric parahydroxybenzaldehyde, by the action of chloroform on an alkaline solution of phenol (Tiemann and Reimer, Ber. 1876, 824; Tiemann and Herzfeld, *ibid.* 1877, 63 and 213):



One part by weight of phenol, with 2 parts of caustic soda, is dissolved in at least 4 parts of water; the solution is heated to 50°-60° in a flask fitted with a reflux condenser, and 2 parts of chloroform are gradually added, shaking continually. The colour of the liquid changes from

yellow to deep red. The reaction is completed by boiling the mixture for half an hour, after which the excess of chloroform is distilled off. The liquid is then acidified with sulphuric acid and steam-distilled, when salicylaldehyde passes over, along with unchanged phenol. The liquid remaining in the retort is filtered hot; on cooling, it deposits crystals of parahydroxybenzaldehyde. The salicylaldehyde is separated from the phenol by shaking an ethereal solution of the two substances with hydrogen sodium sulphite, with which the salicylaldehyde forms a crystalline compound; this is separated, and decomposed by treatment with sodium carbonate or dilute sulphuric acid, when the aldehyde is liberated.

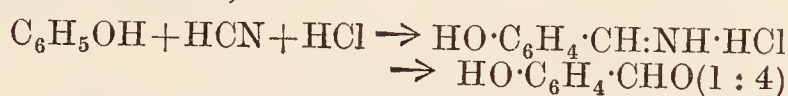
Salicylaldehyde is also formed when salicin $C_{13}H_{18}O_7$ is oxidised with a mixture of potassium dichromate and dilute sulphuric acid (Schiff, *Annalen*, 1869, 150, 193); by the reduction of salicylic acid with sodium amalgam, or electrolytically (H. Weil, *Ber.* 1908, 4147-4150). The electrolytic reduction of the acid to the aldehyde is carried out in aqueous boric acid solution, using a mercury cathode (C. Mettler, *Ber.* 1907, 41, 4148).

Electrolytic preparation of salicylaldehyde from salicylic acid.—Sodium salicylate is reduced electrolytically in the usual type of diaphragm cell with a mercury cathode, sodium sulphate being used as anolyte and a mixture of boric acid and sodium sulphate as catholyte. A current density of 6 amp. per sq. dm. is employed, and the temperature maintained at 15° – 18° ; less aldehyde and more resinous matter are obtained at higher temperatures. The salicylaldehyde produced is fixed as soon as formed by progressive addition of sodium hydrogen sulphite, and is recovered by acid hydrolysis and distillation with steam. The best yield obtained is 55 p.c. of the theoretical (Tesh and Lowy, *Trans. Amer. Electrochem. Soc.* 1924, 45, 325; *Chem. Soc. Abstr.* 1924, 126, i. 646).

Salicylaldehyde is a liquid, with a pleasant aromatic odour. Solidifies at -20° in large crystals, and boils at 196.5° ; sp.gr. 1.1731 at 13.5° . Somewhat soluble in water, miscible in all proportions with alcohol or ether; the aqueous solution gives a strong violet coloration with ferric chloride. By reduction it yields saligenin $C_6H_4(OH)CH_2OH$; on oxidation, salicylic acid. When boiled with acetic anhydride and anhydrous sodium acetate it forms coumarin (*q.v.*). Forms salts with bases: thus $C_6H_4(OK)CHO$ and $C_6H_4(ONa)CHO$; the alkali salts are not decomposed by carbon dioxide. With sulphuryl chloride it yields 5-chlorosalicylaldehyde, melting at 98° (Peratoner, *Gazz. chim. ital.* 1898, 28, i. 197). *Diiodosalicylaldehyde*, mixed with a little *monoiodosalicylaldehyde*, is obtained by treatment in dilute alcoholic solution with iodine and mercuric oxide (Seidel, *J. pr. Chem.* [ii.] 57, 205). By warming together salicylaldehyde, phenol, glacial acetic acid, and concentrated sulphuric acid, Liebermann (*Ber.* 8, 801; 11, 1436) obtained *hydroxy-aurin* $C_{19}H_{14}O_4$, a violet-red colouring matter. Zulkowsky found, among the products of the same reaction, an orange colouring matter which he termed *aurone*, assigning to it the formula $C_{26}H_{20}O_6$. Salicyl-

aldehyde condenses with acetone and its derivatives in the presence of strong sulphuric acid, producing products which are converted on sulphonation into colouring matters which dye in shades from violet-red to blue-grey (D. R. P. 110520; Fabinyi, *Chem. Zentr.* 1900, ii. 301). If the condensation is effected in the presence of caustic soda di-*o*-oxydibenzalacetone results (D. R. P. 110521; Fabinyi, *Chem. Zentr.* 1900, ii. 302). E. Tummeley (*Annalen*, 1889, 251, 174-187) has produced a large number of azo-condensation products.

The isomeric *parahydroxybenzaldehyde* $C_6H_4(OH)CHO$ (1, 4), obtained as described in the foregoing account, crystallises from water in needles melting at 115° – 116° . The solution gives a very faint violet tinge with ferric chloride. It may also be prepared by Gattermann's method, in which anhydrous hydrocyanic acid is condensed by means of hydrogen chloride, with phenol in ether solution,



Metahydroxybenzaldehyde is produced by the reduction of *m*-hydroxybenzoic acid with sodium amalgam. It may be prepared by reducing *m*-nitrobenzaldehyde with tin and hydrochloric acid, and adding sodium nitrite. On addition of concentrated hydrochloric acid the tin double salt crystallises out in white needles, and yields *m*-hydroxybenzaldehyde on being decomposed by water (Ticmann, *Ber.* 1882, 15, 2045). It may also be obtained directly from *m*-amino-benzaldehyde by the diazo-reaction. It melts at 107° and boils at 240° . It gives only a faint violet colour with ferric chloride solution.

For derivatives of salicylaldehyde, see Padoa and Bovini, *Atti R. Accad. Lincei*, 1911, [v.] 20, ii. 712; Torrey and Brewster, *J. Amer. Chem. Soc.* 1913, 35, 426; Lockemann and Lucius, *Ber.* 1913, 46, 1012; Graziani and Bovini, *Atti R. Accad. Lincei*, 1913, [v.] 22, 793; Bovini and Graziani, *Gazz. chim. ital.* 1913, 43, ii. 674; Toschi and Angiolani, *ibid.* 1915, 45, i. 205; Backer, *Rec. trav. chim.* 1915, 34, 187; Henderson and Heilbron, *Chem. Soc. Trans.* 1915, 1746; Chattaway and Ellington, *ibid.* 1916, 592; Chattaway and Hodgson, *ibid.* 1916, 585; Weinhausen, *ibid.* 1918, 585; Bülow and Huss, *Ber.* 1918, 51, 399; Weinland and Barlocher, *ibid.* 1919, 52, [B.] 147; Adams, *J. Amer. Chem. Soc.* 1919, 41, 247; Llorens, *Anal. Fis. Quim.* 1920, 18, 139.

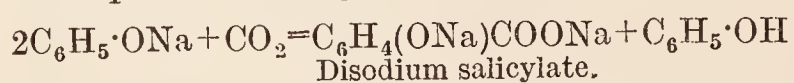
For other derivatives of salicylic aldehyde text-books on pure chemistry must be consulted.

SALICYLIC ACID (*o*-Hydroxybenzoic acid) $C_6H_4(OH)COOH$. It occurs naturally in many plants as the methyl ester (*v. Esters, infra*), and is also found in small quantities in grapes, strawberries, and most fruits; hence it is found to a small extent in most wines (Portes and Desmoulières, *J. Pharm. Chim.* 1901, 14, 342; 1904, 19, 121; *Ann. Chim. anal.* 6, 401; Traphagen and Burke, *J. Amer. Chem. Soc.* 1902, 25, 242; Pellet, *Ann. Chim. anal.* 1907, 12, 10; 1910, 15, 302; Jablin-Gonnet, *ibid.* 1903, 8, 371; Süss, *Chem. Zentr.* 1903, ii. 841; Utz, *ibid.*; Griffiths, *Chem. Soc. Proc.* 1889, 122; Schneegans, *J. Pharm. Chim.* 1895, 2, 452; Windisch, *Zeitsch. Nahr. Genussm.* 1902, 5,

683). It is formed by the fusion of salicylaldehyde with potassium hydroxide (Piria, *Annalen*, 30, 165); and by the same process, from salicin (Gerhardt, *ibid.* 45, 21), coumarin (Delalande, *ibid.* 336), indigo (Cahours, *ibid.* 52, 343), *o*-cresol (Barthe, *ibid.* 154, 360), *o*-toluenesulphonic acid (Wolkow, *Zeitsch. Chem.* 1870, 326), and *m*-bromobenzoic acid (Hübner, *Annalen*, 162, 71). It is also formed by the action of nitrous acid on anthranilic acid (Gerland, *ibid.* 86, 47); by the electrolysis of a solution of benzoic acid in acetic acid (Bargellini and Inghilleri, *Rend. Soc. Chim. di Roma*, 1908, 6, 333), and by exposing solutions of benzoic acid to sunlight in the presence of a ferric salt (Neuberg, *Biochem. Zeitsch.* 1910, 27, 271).

Kolbe and Lautemann (*Annalen*, 115, 201) obtained it by passing carbon dioxide into a heated mixture of sodium and phenol. Kolbe afterwards found that dry sodium phenoxide, prepared from phenol and sodium hydroxide, could be substituted for the sodium and phenol in the foregoing reaction, and patented the following process, by which salicylic acid has been manufactured on a large scale (*J. pr. Chem.* 10, [ii.] 93; *D. R. P.* 426; *Frdl. i.* 229).

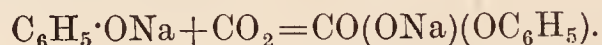
Crystallised phenol is dissolved in the equivalent quantity of concentrated sodium hydroxide and the solution is evaporated to dryness in shallow iron vessels, stirring thoroughly to prevent charring, and finally grinding it with a heavy pestle to a dry powder; or equivalent quantities of phenol and caustic soda with about 5 p.c. of sodium sulphite are intimately mixed in a specially constructed grinding ball-mill and heated to 250°–280°. The dry sodium phenoxide $C_6H_5 \cdot CNa$, which is always of a reddish-yellow colour and very hygroscopic, is heated in a metal retort at first to 100°, and a current of dry heated carbon dioxide is passed in, constantly stirring the mass. The temperature is gradually raised, so that after a lapse of several hours it rises to 180°. After the heating has been continued for some time phenol begins to distil over, at first in small quantity, afterwards more abundantly. Finally the temperature is raised to 200°, and the operation, which lasts from 6 to 8 hours, is interrupted when no more phenol distils over at that temperature. It is necessary to keep up a rapid current of heated carbon dioxide in order that the liberated phenol may be removed as rapidly as possible from the retort, otherwise the mass cakes together, preventing further absorption. Half of the phenol originally present as phenoxide distils over during the process. The reaction takes place according to the equation



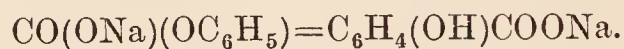
The greyish-white mass of disodium salicylate remaining in the retort is, after cooling, dissolved in water and freed from resinous matters and coloured impurities by fractional precipitation with hydrochloric or sulphuric acid, after which the salicylic acid itself is precipitated by a further addition of the mineral acid. Or the dry sodium phenoxide is placed in a rotating autoclave and treated with carbon dioxide without heating. When the gas ceases to be absorbed the pressure of the carbon dioxide is increased to more than 100 lbs. per sq. in.,

and the autoclave heated to 120°–140°. The crude sodium salicylate is dissolved in water, the solution just acidified with sulphuric acid passed down a column of granulated zinc and after heating to 80°–100° down a tower containing a mixture of charcoal and zinc. On adding acid to the filtrate colourless salicylic acid is obtained (Everitt, *Eng. Pats.* 105611, 105612, 105613, 105614).

The reaction which occurs was first explained by R. Schmitt (*J. pr. Chem.* [ii.] 31, 397), who showed that when carbon dioxide acts on sodium phenoxide in the cold, sodium phenyl carbonate is formed



When this compound is heated under ordinary pressures carbon dioxide is given off and only a small quantity of salicylic acid is formed, but when it is heated under pressure at 120°–140° it is converted quantitatively into the isomeric sodium salicylate



In this process the whole of the phenol is converted into salicylic acid, and it has the further advantage that the temperature employed being lower, a purer product is at once obtained. For theory of reaction, *v.* Moll van Charante, *Rec. trav. chim.* 1908, 27, 58; *Chem. Soc. Abstr.* 1906, i. 665; Tijmstra, *Ber.* 1905, 38, 1375; de Bruyn and Tijmstra, *Rec. trav. chim.* 1904, 23, 385. Schmitt describes (*D. R. P.* 29939; *Frdl. i.* 233) three methods of carrying out the process: (1) The dry alkaline phenoxide (phenoxides of the alkaline earths may be substituted) is treated with carbon dioxide at ordinary temperature and pressure as long as absorption takes place, and the resulting compound is then heated in an autoclave for some hours at 120°–140°. (2) Carbon dioxide is pumped under pressure into an autoclave containing the alkaline phenoxide, cooling during the process, after which the autoclave is closed and left for some hours in order to allow the formation of the alkaline phenylcarbonate to be complete. It is then heated. (3) Instead of pumping in the carbon dioxide it is introduced in the form of solid carbon dioxide, and the autoclave is then quickly closed. The rest of the process is as in the preceding case (*v.* also *J. Soc. Chem. Ind.* 1885, 551). It has since been found, however (*D. R. P.* 38742; *Eng. Pat.* 7801; *J. Soc. Chem. Ind.* 1886, 501; *Frdl. i.* 234), that the process may be simplified by subjecting the alkaline phenoxide to the action of carbon dioxide under pressure at a temperature of 120°–140°, instead of at ordinary temperatures. These limits of temperature must not be exceeded, otherwise phenol is split off and the reaction takes place according to Kolbe's process. The alkaline phenyl-carbonate is converted, at the moment of its formation, into salicylate, thus completing the action in one stage instead of in two. Marasse (*Eng. Pat.* 17002; *D. R. PP.* 77932, 78708; *J. Soc. Chem. Ind.* 1893, 1055) heats an intimate mixture of phenol and potassium carbonate at 130°–160° and treats the product with the requisite quantity of carbon dioxide. Schering (*D. R. P.* 133500; *Chem. Soc. Abstr.* 1903, i. 343) substitutes the product obtained by the fusion of alkali benzene sulphonate and

alkali hydroxide, for the sodium phenate in Kolbe's process. It is claimed that thus oxidation is hindered and alkali economised. Lederer (D. R. P. 80747; *Frdl.* iv. 151) heats the product obtained by condensing *o*-cresol and chloracetic acid with alkali at 260°–270°. On the course of the Kolbe reaction see C. H. Sluiter, *Ber.* 1912, 45, 59, 3008; and S. Tijmstra, *ibid.* 2837.

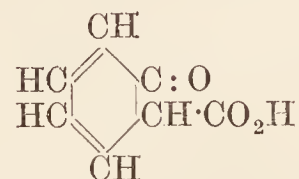
Salicylic acid is formed, together with *p*-hydroxybenzoic acid, the latter predominating, when an alkaline solution of phenol is boiled with carbon tetrachloride: $C_6H_5\cdot ONa + 5NaOH + CCl_4 = C_6H_4(ONa)COONa + 4NaCl + 3H_2O$ (Reimer and Tiemann, *Ber.* 1876, 9, 1285). Sodium salicylate is obtained by electrolysis with 5–8 amps. per sq. decm. in the anode compartment a mixture of *o*-cresol, and caustic soda at 240°–250°, nickel or nickel-steel or iron being used as electrodes (Pomilio, *Eng. Pat.* 103709).

Salicylic acid is now prepared chiefly by the action of carbon dioxide on heated sodium phenoxide. There are three grades of acid on the market: (1) ordinary acid, the cheapest; (2) natural acid, the most expensive, but free from *p*-hydroxybenzoic acid, which is not entirely destitute of harmful physiological effects; (3) an intermediate acid, physiologically pure, and free from *p*-cresotic acid. The crude acid obtained by any of the above processes may be purified by neutralising a hot aqueous solution with calcium carbonate, allowing it to cool and filtering off the calcium salt. This is then recrystallised from hot water until colourless, decomposed with hydrochloric acid, washed with cold water, and recrystallised from dilute spirit (Henderson, *J. Soc. Chem. Ind.* 1890, 591). For purification by means of stannous chloride or other tin salts, v. Hofmann (D. R. PP. 65131, 67893; *Frdl.* iii. 826, 827). For special purposes, salicylic acid can be purified by fractional crystallisation of the silver salt with silver nitrate, any cresol derivative accumulating in the last fractions (*Chemist and Druggist*, 40, 590). The chief impurities in commercial salicylic acid are phenol, cresotic acid, *p*-hydroxybenzoic acid, and α -hydroxyisophthalic acid. According to Henderson (*l.c.*) and B. Fischer (*Pharm. Zeit. f. Russ.* 1889, 28, 378; *J. Pharm. Chim.* 20, [5] 258) the presence of the two last-named compounds is due to unregulated temperature in the manufacturing process. Up to 150°, pure potassium salicylate is obtained, above 150° potassium *p*-hydroxybenzoate is also formed, and at 220° the latter compound is the main product. If alkali is present, *p*-hydroxybenzoic acid is produced. At a high temperature α -hydroxyisophthalic acid is formed by the action of carbon dioxide on the potassium salicylate already formed. In a well-regulated process, not more than 0.4 p.c. of these two acids is formed. To test for these impurities, 0.5 gm. of the acid is triturated in a mortar with 5 c.c. water and transferred to a test-tube. Two drops of a 2 p.c. solution of furfuraldehyde are added, and then 3 c.c. concentrated sulphuric acid without mixing. A brown ring shows the presence of *o*-cresotic acid, a faint violet ring that of *m*- or *p*-cresotic acids, and a blue ring above a yellow one indicates phenol (Carletti, *Boll. chim. farm.* 1907, 46, 421; Engelhardt and Jones, *J. Soc. Chem. Ind.* 1908, 1131). For other

tests v. B. Fischer, *l.c.*; Ewell and Prescott, *Analyst*, 1888, 13, 237; *Pharm. J.* 19, [3] 380; Ferraro, *Boll. chim. farm.* 1908, 47, 789; H. L. Smith, *Analyst*, 1916, 41, 3.

Properties.—Salicylic acid crystallises from hot water in slender needles and by spontaneous evaporation of its alcoholic solution, in monoclinic prisms (Marignac, *J.* 1885, 484). Very soluble in alcohol and ether, sparingly soluble in cold, readily in hot water (Walker and Wood, *Chem. Soc. Trans.* 1898, 620; Savarro, *Atti R. Accad. Sci. Torino*, 1913, 48, 948). For influence of sodium salts on the solubility, v. Philip, *Chem. Soc. Trans.* 1905, 987. M.p. 159°; 158.5° (corr.) (H. L. Smith, *l.c.*). The presence of 1 p.c. of *p*-hydroxybenzoic acid lowers the m.p. to 155°–156°. The m.p. required by the *Brit. Pharm.* is 156°–157°. Heat of combustion, &c., v. Berthelot and Recoura, *Compt. rend.* 104, 1571; *Ann. Chim. Phys.* 13, [6] 320; Stohmann, *J. pr. Chem.* 50, [2] 389; Delépine and Rivals, *Compt. rend.* 1899, 129, 520. When carefully heated salicylic acid sublimes without decomposition, but when quickly distilled breaks up into phenol and carbon dioxide (Graebe, *Annalen*, 139, 143). According to Graebe and Eichengrün (*ibid.* 1892, 269, 323) when heated at 195°–220° it splits up mainly into salol and xanthone. According to Christiansen (*Zeitsch. physikal. Chem.* 1916, 91, 701) it is completely dissociated at 203° into phenol and carbon dioxide. Cf. Baur, *Schweiz. Chem. Zeit.* 1918, ii. 25; *Zeitsch. physikal. Chem.* 1918, 93, 240; Orthner, *ibid.* 1918, 93, 220–236. Chlorine reacts with salicylic acid to form mono- and disubstituted products (Tarugi, *Gazz. chim. ital.* 1900, 30, 487); for action of bromine, v. *Volumetric estimation*. Cold nitric acid reacts to form 5-nitrosalicylic acid, and fuming nitric acid to produce picric acid. By warming with phosphorus pentoxide, salicylmetaphosphoric acid is formed, which when heated with alcohols or phenols yields the esters of salicylic acid, but with 2 mols. of phenols at a higher temperature the dyestuff *salicyleine* is formed (Schultze, D. R. PP. 75830, 85565, 86319; *Frdl.* iv. 154, 155, 198). On reduction with sodium and amyl alcohol pimelic acid is the chief product (Einhorn and Willstätter, *Ber.* 1893, 2913; 1894, 331); reduction with sodium amalgam in the presence of boric acid yields salicylaldehyde (Weil, *ibid.* 1908, 41, 4147; Mettler, *ibid.* 4148). On standing for a long time solutions of salicylic acid develop a fungoid growth, which decomposes the acid; more rapidly on the addition of a little ferric chloride (Lott, *J. Soc. Chem. Ind.* 1903, 198).

Salicylic acid behaves in alkaline solution as a monobasic acid in retarding the destruction of dextrose, whereas *m*- and *p*-hydroxybenzoic acids behave as dibasic acids. Waterman regards this fact as supporting Brunner's constitutional formula for salicylic acid as



(*Proc. K. Akad. Wetensh. Amsterdam*, 1918, 20, 581).

Salicylic acid is extensively used as a food

preservative. It is also used in medicine as an intestinal antiseptic, and in the treatment of gout and rheumatism. It has toxic properties and its salts cause albuminuria. It is excreted partly unchanged and partly as salicyluric acid (Bondzynski, Chem. Zentr. 1896, ii. 1039; cf. Jacoby, Biochem. Zeitsch. 1908, 9, 522, 527; Rockwood, J. Biol. Chem. 1909, 6). Salicylic acid dissolved in flexible collodion is used as a corn solvent.

Salicylic acid which is intended for use in medicine should be white and should show the proper melting-point. It should dissolve in cold concentrated sulphuric acid to form a colourless solution, and should leave no residue on ignition. Another method of testing the acid consists in dissolving the sample in absolute alcohol, allowing the solution to evaporate spontaneously and observing the points of the crystals formed: these will be colourless if the acid is pure, violet or pink if it contains iron, yellow or brown if resinous impurities are present.

Salicylic acid is used in the production of azo- dyes, such as *flavazol* and *chrysamin*. It influences the shade in the direction of yellow and tends to increase its fastness to light, though no dyestuff containing it is fast to chlorine (Bona, Farb. Zeit. 5, 120). *Azo- dyestuffs*, v. Gebek, Annalen, 251, 188; Kostanecki and Zibell, Ber. 1891, 1695; Landsteiner, Chem. Zentr. 1895, ii. 891; Paul, Zeitsch. angew. Chem. 1896, 679; Grandmougin, Guisan and Freimann, Ber. 1907, 40, 3450; Chem. Zentr. 1908, ii. 310; J. pr. Chem. 1908, 78, [ii.] 384; Nietzki, D. R. P. 44170; Frdl. ii. 323; Bayer & Co. D. R. PP. 61950, 31658; Ber. 1892; Ref. 530; Frdl. i. 465; Bad. Anil. u. Sod. Fabr. D. R. P. 58893; Ber. 1892, Ref. 928; Cassella & Co. D. R. P. 66351; Frdl. iii. 677; Leonhardt & Co. D. R. P. 38735; Frdl. i. 510. *Triphenylmethane dyestuffs*, v. Höchster Farb. D. R. P. 75803; Frdl. iv. 197.

It has also been recommended as a preservative in thiosulphate solutions (Bornträger, Zeitsch. anal. Chem. 27, 641).

ESTERS.

Methyl salicylate, *Oil of Wintergreen*, *Gaultheria oil*, $C_6H_4(OH)COOCH_3$. The chief natural sources of methyl salicylate are the leaves of *Gaultheria procumbens*, and the bark of the sweet birch (*Betula lenta*) (Power and Kleber, Pharm. Rundschau, 1895, 13, 228). In other plants it occurs chiefly as the glucoside, *Gaultherin*, which is hydrolysed to dextrose and methyl salicylate by the soluble ferment *betulase*. The following are the more important plants in which methyl salicylate is found: *Polygala Senega* (Linn.), *P. Baldwini* (Nutt.), *P. Variabilis* (H. B. & K.), *P. Javana* (DC.), *P. oleifera* (Heck.), *P. serpyllacea* (Weihe), *P. calcarea* (Schultz), *P. vulgaris* (Linn.), *Gaultheria procumbens* (Linn.), *G. fragrantissima* (Wall.), *G. leucocarpa* (Blume.), *Betula lenta* (Linn.), *Spiraea Ulmaria* (Linn.), *Erythroxylum Coca* (Lam.), *Hypopitys multiflora* (Scop.), *Camellia Thea* (Link.), *Acacia caesia* (Wight and Arn.), *A. pluricapitata* (Steud.), *A. pennata* (Willd.), *A. Farnesiana* (Willd.) and *Viola tricolor* (Linn.). (Kremers and James, Pharm. Rev. 1898, 16, 100; Bourquelot, Compt. rend. 1894, 119, 802;

J. Soc. Chem. Ind. 1899, 1153). It can be prepared synthetically by boiling a mixture of salicylic acid, sulphuric acid, and methyl alcohol under a reflux apparatus (Cahours, Ann. Chim. Phys. 10, [3] 327). Colourless oil, b.p. 222.2° , sp.gr. $4^\circ/4^\circ$ 1.1992, $15^\circ/15^\circ$ 1.189 (Perkin, Chem. Soc. Trans. 1896, 1238). In presence of water or dilute acids or alkalis it becomes coloured on exposure to air and sunlight, the tint varying from light yellow to reddish brown. Active oxidising agents effect the same change in the dark. Combines with thiocarbamide; long needles (Taylor, Chem. Soc. Trans. 1917, 661). For detection of free salicylic acid, v. Pharm. Centr. 1892, 33, 40; Zeitsch. anal. Chem. 32, 363. For estimation, v. Gibbs, J. Amer. Chem. Soc. 1908, 30, 1465. For a method of examining methyl salicylate, see Albright, J. Amer. Chem. Soc. 1917, 39, 820.

Ethyl salicylate $C_6H_4(OH)COOC_2H_5$. Prepared by the action of ethyl alcohol and sulphuric or hydrochloric acids on salicylic acid (Cahours, Annalen, 52, 332; 74, 314; Göttig, Ber. 1876, 1473). B.p. 233.5° – 234° ; sp.gr. $4^\circ/4^\circ$, 1.1470; $15^\circ/15^\circ$, 1.372 (Perkin, l.c.). When heated to 300° it decomposes into phenol, ethylene, and carbon dioxide (A. Colson, Compt. rend. 1909, 148, 643). Physiological action, v. Houghton, Amer. J. Physiol. 1905, 13, 331.

Allyl salicylate, v. Akt. Ges. f. Anilfabr; J. Soc. Chem. Ind. 1910, 1332; D. R. P. 244208. It is a colourless liquid with a cabbage-like odour, boiling at 247° – 250° , sp.gr. 15° , 1.10. Its alcoholic solution develops a violet colour with ferric chloride. Used medicinally and as a perfume.

Phenyl salicylate (*Salol*) $C_6H_4(OH)COOC_6H_5$. Prepared by the action of the chlorides or oxychlorides of phosphorus on a mixture of salicylic acid or a salicylate with phenol (Nencki, Eng. Pat. 8018; D. R. PP. 38973, 43713, 1622; J. Soc. Chem. Ind. 1886, 577; 1887, 561; Frdl. i. 237; ii. 314). Eckenroth (D. R. P. 39184; J. Soc. Chem. Ind. 1886, 677; Frdl. i. 240) has obtained it by the action of phosgene gas on a mixture of sodium salicylate and sodium phenate. Byk (Eng. Pat. 23449; J. Soc. Chem. Ind. 1894, 274) substitutes a mixture of phosphoric anhydride and phosphoric acid for phosphorus oxychloride. Emert (Eng. Pat. 14224; D. R. P. 62276; J. Soc. Chem. Ind. 1891, 1026; Frdl. iii. 835) heats salicylic acid at 220° in an atmosphere of carbon dioxide. Salol has also been prepared by the interaction of polysalicylide and phenol (Akt. Ges. f. Anilfabr. D. R. P. 73452; Frdl. iii. 835). The product obtained by these methods is usually steam distilled and finally purified by recrystallisation from dilute alcohol. Rhombic crystals, m.p. 43° ; soluble in most organic solvents, but insoluble in water (Lusini, L'Orosi, 1903, 26, 89). When taken internally, it passes unaltered through the stomach, but is hydrolysed in the duodenum by the pancreatic ferment into phenol and salicylic acid (J. Soc. Chem. Ind. 1886, 577; v. also Humnicki, Chem. Zentr. 1899, i. 369; Bull. Acad. Sci. Cracow, 1908, 841; Lusini, L'Orosi, 1903, 26, 47). To avoid this resolution into phenol, *p*-aminophenylacetyl salicylate has been introduced into commerce under the name of *salophen* (van Eck, Chem. Weekblad. 1907, 4, 539; Cohn, J. pr. Chem.

61, [2] 550; Bayer & Co. D. R. PP. 62533, 60289; Frdl. iii. 836; Brewster, J. Amer. Chem. Soc. 1918, 40, 1136). This is hydrolysed into salicylic acid and *p*-aminophenol, an innocuous product which is eliminated without further change. *Salolchlorocarbonate*, v. F. Bayer & Co. D. R. PP. 109933, 114025, 118537; Chem. Soc. Abstr. 1901, ii. 697. For estimation of salol, v. Squire and Caines, Pharm. J. 1905, [iv.] 20, 720; in surgical dressings, Telle, J. Pharm. Chim. 1901, 13, 49; 14, 289; in mouth washes, &c., Beythien and Athenstadt, Zeitsch. Nahr. Genussm. 1907, 14, 392. For the estimation of salol in mixtures containing phenacetin and acetanilide, see W. O. Emery, G. C. Spencer, and C. C. Le Febore, J. Ind. Eng. Chem. 1915, 7, 681; and B. Salkorer, Amer. J. Pharm. 1916, 88, 484. *Phenyl acetylsalicylate*, *Acetyl-salol*, *Vesipyrin* (Knebel, J. pr. Chem. 1891, 43, 378; Zernik, Apoth. Zeit. 1907, 22, 152) is a white tasteless powder, m.p. 97°. The name *salol* is now often used to mean the compounds formed by the condensation of a substituted phenol with a substituted hydroxy-acid. *Halogenated salols*, v. Eckenroth and Wolf, Ber. 1893, 3463; Kauschke, J. pr. Chem. 1895, 51, [2] 210; Kolbe, Eng. Pat. 6749; J. Soc. Chem. Ind. 1894, 275). *Cresalols* are the compounds formed by condensation of the cresols with salicylic acid (Kolbe, Eng. Pats. 13169, 17221; J. Soc. Chem. Ind. 1889, 817; 1892, 58). α - and β -*Naphthyl salicylates*, *Salinaphthols*, known respectively as *Alphol* and *Betol*, are prepared in a similar manner (Byk, l.c.). *Betol* is used as an intestinal antiseptic in ague and articular rheumatism. For distinction of *alphol* from *betol*, v. Dragendorff, Arch. Pharm. 1895, 233, 612.

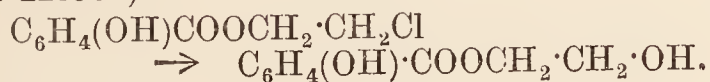
Phenacyl salicylate, obtained by the action of phenacyl bromide (ω -bromoacetophenone) on a boiling alcoholic solution of salicylic acid, m.p. 110° (Rather and Reid, J. Amer. Chem. Soc. 1919, 41, 75).

Benzyl salicylate, v. Akt. Ges. f. Anilfabr. D. R. PP. 119463, 144002; Chem. Soc. Abstr. 1901, i. 712; Chem. Zentr. 1903, ii. 1040. For the thiocarbamide compound, see Taylor, Chem. Soc. Trans. 1917, 111, 662. Fine needles, m.p. 144°–145°.

Fenchyl salicylate, m.p. 51°, is of therapeutic value and is prepared from fenchyl alcohol, and salicylic acid or methyl salicylate (Chem. Fabr. Keresety, Wolf & Co., D. R. P. 253756).

Ethylhydrocupreine salicylate, a colourless, tasteless powder, m.p. 50°, is prepared by digesting ethylhydrocupreine with phenyl salicylate for six hours at 130°–135° (Swiss Pat. 63031).

The salicyl monoglycol esters are obtained by the action of mild saponifying agents or by the action of the salts of weak acids (e.g. sodium acetate, sodium phosphate) on the esters of salicylic acid and glycolmonochlorhydrin (D. R. P. 225984)



SALTS.

The monobasic salicylates of the formula $\text{C}_6\text{H}_4(\text{OH})\text{COOR}$ are mostly soluble in water, the dibasic salicylates $\text{C}_6\text{H}_4(\text{OR})\text{COOR}$ being mostly insoluble (Piria, J. 1885, 485; Milone, Gazz. chim. ital. 15, 219).

Sodium salicylate $\text{NaC}_7\text{H}_5\text{O}_3\cdot\text{H}_2\text{O}$ crystal-

lises in colourless plates, very soluble in water and alcohol (Massol, Ann. Chim. Phys. [7] 1, 217; de Coninck, Bull. Acad. roy. Belg. 1907, 651). Also known anhydrous (Chemist and Druggist, 40, 590), and with $6\text{H}_2\text{O}$ (Romyn, Ned. Tydschr. Pharm. 1896, 111). Heated in air to 300° it decomposes into the disodium salt, carbon dioxide and phenol, but in an atmosphere of carbon dioxide 4-hydroxyisophthalic acid $\text{C}_8\text{H}_6\text{O}_5$, and hydroxytrimesic acid $\text{C}_9\text{H}_6\text{O}_7$ are formed. Taken internally, sodium salicylate causes increased katabolism of proteid material (Goodbody, J. Physiol. 1900, 25, 399; Baldoni, Arch. exp. Path. Pharm. Suppl. 1908, 54). For assay of sodium salt, v. Alcock, Pharm. J. 1906, 23, 597. For double salt with sodium lactate, v. Tollner, D. R. P. 84378; Frdl. iv. 1188.

Potassium salicylate $\text{KC}_7\text{H}_5\text{O}_3\cdot\frac{1}{2}\text{H}_2\text{O}$. When heated to 200° it changes into the dibasic salt of *p*-hydroxybenzoic acid, carbon dioxide, and phenol (Ost, J. pr. Chem. [2] 11, 329).

Lithium salicylate $\text{LiC}_7\text{H}_5\text{O}_3$. White crystalline powder, soluble in water and alcohol. Heated to 300°, it is transformed into the dibasic salt, no para-compound being produced. Used in cases of chronic or acute rheumatism.

Ammonium salicylate $\text{NH}_4\text{C}_7\text{H}_5\text{O}_3$, v. Saban-jew, J. Russ. Phys. Chem. Soc. 31, 380; Marignac, J. 1855, 485.

Salicylates of the alkaline earths, v. Milone, l.c.; Tarugi and Checchi, Gazz. chim. ital. 1901, 31, ii. 417; Echsner de Coninck, Rev. Gén. Chim. pure Appl. 1914, 17, 72.

Ferrous salicylate $\text{Fe}(\text{CO}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH})_2$ is a reddish-violet amorphous substance.

Ferric salicylate $\text{Fe}(\text{C}_7\text{H}_5\text{O}_3)_3$. Formed as a brown precipitate on mixing ferric chloride and salicylic acid; quickly acquires a violet colour. For theory of reaction, v. Rosenthaler, Arch. Pharm. 1904, 242, 563; Hopfgartner, Monatsh. 1908, 28, 689; Desmoulières, J. Pharm. Chim. 1902, [vi.] 16, 241; Weinland and Herz, Annalen, 1913, 400, 219; Weinland and Zimmermann, Arch. Pharm. 1917, 255, 204).

Chromous salicylate $\text{C}_6\text{H}_4\langle\text{CO}_2\rangle\text{Cr}\cdot 3\text{H}_2\text{O}$.

Prepared by reducing chrome alum solution with zinc and hydrochloric acid and adding sodium salicylate solution free from air, forms small red crystals which rapidly oxidise and become greenish-grey in the air (Scagliarini, Atti R. Accad. Lincei, 1918, [v.] 27, ii. 87).

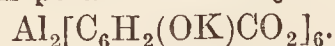
Aluminium salicylate $\text{Al}_2(\text{C}_7\text{H}_5\text{O}_3)_6\cdot 3\text{H}_2\text{O}$. Prepared by adding a solution of an aluminium salt to that of sodium salicylate. Used as a dusting powder in catarrhal affections of the nose and pharynx under the name of *Salumen* (Allen's Commercial Organic Analysis, 1910, iii. 488).

Aluminium ammonium salicylate



A neutral soluble salt more stable in solution than in the dry state. Used as an astringent wash for the throat and nose under the name of *Soluble Salumen* (Heyden Nachf., D. R. P. 81819; Frdl. iv. 1190; Allen, l.c.).

Aluminium potassium salicylate



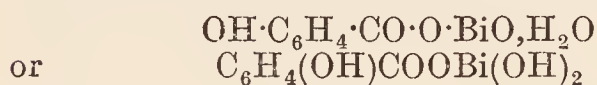
Used as a combined antiseptic and astringent under the name of *Alkasal* or *Alkasol* (Athenstadt, D. R. P. 78903; Frdl. iv. 1189; Allen, l.c.).

Mercuric salicylate $\text{Hg}(\text{C}_7\text{H}_5\text{O}_3)_2$. Prepared by adding a solution of mercuric acetate to one of sodium salicylate acidified with acetic acid (Buroni, Gazz. chim. ital. 1902, 32, ii. 311). On boiling the solution there is formed the anhydride of *hydroxymercurisalicylic acid*



(Buroni, *ibid.* 305; Lintner, Zeitsch. angew. Chem. 1900, 707). According to Lajoux (J. Pharm. Chim. 1907, 17, 412) the latter has the constitution $\text{C}_6\text{H}_4 < \begin{smallmatrix} \text{CO}_2 \\ \text{O} \end{smallmatrix} > \text{Hg}$, and it may be prepared by gradually adding freshly precipitated yellow mercuric oxide to a boiling solution of salicylic acid (Lajoux and Grandval, J. Pharm. Chim. v. 20, 5; Compt. rend. 117, 44; Echsner de Coninck, Rev. Gén. Chim. 1914, 17, 125; cf., however, Lajoux, J. Pharm. Chim. 1915, [vii.] 11, 279, who confirms Buroni's view. For compounds with organic acids, see Kerb, D. R. P. 247625.

Bismuth salicylate. The basic bismuth salicylate of commerce, which is extensively used in medicine, is more correctly *bismuthyl salicylate*



(Martinotti and Cornelio, Boll. chim. farm. 1901, 40, 141; v. also Causse, Compt. rend. 113, 547). It may be prepared by saturating 40 c.c. of concentrated hydrochloric acid with bismuth oxide in the presence of 500 c.c. of saturated sodium chloride solution; to another 500 c.c. of brine 9 grms. of sodium hydroxide and 22 grms. of sodium salicylate are added. The two solutions are mixed, and the precipitate washed with water containing a few drops of nitric acid (Causse, *l.c.*). Microscopical prisms (v. also Fischer and Grützner, Arch. Pharm. 231, 680). Causse (Compt. rend. 112, 1220) has described a bismuth salicylate having the composition $\text{Bi}(\text{C}_7\text{H}_5\text{O}_3)_3 \cdot 4\text{H}_2\text{O}$. Thibault (Ann. Chim. 1902, [vii.] 25, 268; J. Pharm. Chim. 1901, 14, 32; Bull. Soc. chim. 1901, iii. 25, 794) has prepared a bismuth salicylate having the composition $\text{Bi}_2\text{O}_3(\text{C}_7\text{H}_6\text{O}_3)$. Bismuth disalicylate $\text{OH} \cdot \text{Bi}(\text{O} \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{OH})_2$ or $\text{O}[\text{Bi}(\text{O} \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{OH})_2]_2$ is prepared by adding crystalline bismuth nitrate to an aqueous solution of sodium salicylate, and after thorough mixing, the free acid is extracted with an indifferent solvent (Chem. Farb. v. Heyden, Eng. Pat. 19375; D. R. P. 168408; Chem. Soc. Abstr. 1906, i. 665).

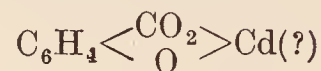
Estimation of bismuth salicylate, v. Lyon, Pharm. J. 1904, iv. 18, 219; Harrison, *ibid.* 1908, 81, 349; Kollo, Proc. Amer. Pharm. Assoc. 1899, 719.

Bismuth cerium salicylate. An insoluble pink powder used in the treatment of diseases of the gastric and intestinal mucous membranes (Allen, iii. 491).

Cerous salicylate $\text{Ce}_2(\text{C}_7\text{H}_5\text{O}_3)_6 \cdot 3\text{H}_2\text{O}$ (v. Morgan and Cahen, Pharm. J. 1908, 78, 428).

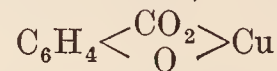
Cadmium salicylate $\text{Cd}(\text{C}_7\text{H}_5\text{O}_3)_2$. Prepared by treating salicylic acid with cadmium oxide or carbonate. Lustrous crystals; possesses valuable antiseptic properties (Caesaris, L'Orosi, 17, 262). Needles or plates as monohydrate. De-

composed by hot water with liberation of salicylic acid and formation of a basic salt



(De Coninck, Bull. Soc. chim. 1914, [iv.] 15, 608).

Copper salicylate, v. Ley and Erler (Zeitsch. anorg. Chem. 1908, 56, 401). Gives a basic salt

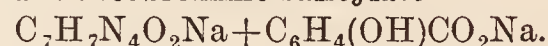


on boiling its aqueous solution.

Salicylates of the rare earths, v. Zimmer & Co. (Eng. Pat. 13459; J. Soc. Chem. Ind. 1896, 606).

DERIVATIVES.

Sodium theobromine-salicylate



Known as *Diuretin*. Prepared by mixing aqueous solutions of molecular proportions of sodium theobromine and sodium salicylate, and evaporating to dryness. Used as a diuretic in cases of scarlet fever, nephritis, &c. (J. Soc. Chem. Ind. 1890, 544). *Barutine* (Brat, Chem. Zentr. 1905, ii. 1189; Akt. ges. f. Anilf. D. R. P. 167140; Chem. Soc. Abstr. 1906, i. 692) is the corresponding barium compound and *Uropherin* the lithium compound.

Bornyl salicylate $\text{C}_{10}\text{H}_{17}\text{O} \cdot \text{CO} \cdot \text{C}_6\text{H}_4\text{OH}$. Known as *Salit*. Prepared by heating a mixture of French oil of turpentine and salicylic acid, has b.p. 171° – $173^\circ/5$ mm. (Tardy, J. Pharm. Chim. 1904, 20, [ii.] 57; Farb. v. Heyden, D. R. P. 175097; Chem. Soc. Abstr. 1907, i. 429).

Quinine salicylate $\text{C}_{20}\text{H}_{24}\text{N}_2\text{O}_2 \cdot \text{C}_7\text{H}_6\text{O}_3 \cdot \text{H}_2\text{O}$. White needles, used as an antipyretic in typhus and as a remedy for rheumatism and gout. Soluble in 225 parts of cold water, and 20 parts of 90 p.c. alcohol.

Hydroquinine salicylate, large colourless crystals, m.p. 115° – 119° is prepared by heating hydroquinine with salol during six hours at 130° – 140° (Vereinigte Chininfabriken Zimmer & Co., D. R. P. 250379).

Salicyl derivatives of the Cinchona alkaloids, v. F. Bayer & Co. D. R. P. 137207; Chem. Soc. Abstr. 1903, i. 513.

Antipyrine salicylate $\text{C}_{11}\text{H}_{12}\text{N}_2\text{O} \cdot \text{C}_7\text{H}_6\text{O}_3$ (*Salipyrin*). Crystalline odourless powder, having a pleasant taste and possessing the properties of its constituents, m.p. 91° *circa* (Patein and Dufau, Bull. Soc. chim. 15, [3] 847; Schuyten, Chem. Zentr. 1899, ii. 38; 1901, ii. 484; Bourgeois, Rec. trav. chim. 18, 451). For estimation, v. Altschul, Pharm. Centr. Halle. 1893, 33, 61.

Constitution of salipyrine.—From determinations of the effect of adding salipyrine to a suspension of silver salicylate in saturated salicylic acid solution in contact with a silver electrode on the potential of the system against a normal calomel electrode, it is deduced that, although salipyrine is largely hydrolysed in solution into salicylic acid and antipyrine, the undissociated salipyrine consists of a complex additive compound such as



(S. Bodforss and A. Guthe, Ber. 1924, 57, 842; J. Soc. Chem. Ind. 1924, 43, B. 534).

Tolypyrine salicylate, *Tolysal*, m.p. 91° .

Resembles salipyrin. **Colchicine salicylate**, **Colchisal**, is used in the treatment of arthritis, rheumatism, and gout: yellow amorphous powder, soluble in water, alcohol, and ether. A mixture of colchicine and methyl salicylate is also called *colchisal*. **Saloquinone**, the quinine ester of salicylic acid $C_6H_4(OH)CO_2C_{20}H_{23}N_2O$, is used as an analgesic. **Rheumatine**, the salicylate of saloquinone, is used in the treatment of rheumatism. **Phenolphthalein disalicylate**, *v.* Knoll & Co., D. R. P. 212892; Chem. Soc. Abstr. 1909, i. 932. **Brucine salicylate**, *v.* Hilditch, Chem. Soc. Trans. 1908, 1391. **Hydroxyethyl salicylate**, *v.* Bad. Anil. u. Sod. Fab. D. R. P. 173776; Chem. Soc. Abstr. 1906, i. 957. **Alkyloxyalkyl esters**, *v.* F. Bayer & Co., D. R. P. 146849; Chem. Soc. Abstr. 1905, i. 318. **Acylsalicylic acids**, *v.* Lassar Cohn and Löwenstein, Ber. 1908, 41, 3360; Einhorn, Rothlauf, and Seuffert, *ibid.* 1911, 44, 3309; Farb. v. F. Bayer, D. R. PP. 201325, 201326, Chem. Soc. Abstr. 1908, i. 984. **Alkyl- and aryloxyacylsalicylic acids**, *v.* Farb. v. Heyden, D. R. P. 221385; J. Soc. Chem. Ind. 1910, 650. **Carboxyalkylsalicylic acids**, *v.* Einhorn, Eng. Pat. 24009; J. Soc. Chem. Ind. 1910, 649. **Alkyl-oxyethyl ethers**, *v.* Farbenfab. v. Elberfeld Co., U.S. Pat. 706018; D. R. P. 137585; J. Soc. Chem. Ind. 1902, 1154. **Alkyloxyalkylidene esters**, *v.* U.S. Pat. 740628; J. Soc. Chem. Ind. 1903, 1306. **Alkylaminoalkyl esters**, *v.* Meister, Lucius and Bruning, D. R. P. 188571; J. Soc. Chem. Ind. 1908, 644. **Benzoylmethyl salicylate**, **Salhypnone**, prepared from sodium salicylate and bromacetophenone, m.p. 113° – 114° (Pharm. Centr. H. 37, 103). **Pyridine salicylate**, colourless tablets and prisms, m.p. 60° ; pyridine hydrogen salicylate A_2Py , thick tablets, m.p. 89° (Pfeiffer, Ber. 1914, 47, 1580). **Piperidine salicylate**, *v.* Hewitt, Eng. Pat. 19823; J. Soc. Chem. Ind. 1899, 855. **Glyceryl ester**, *v.* Sorger, Eng. Pat. 3367; U.S. Pat. 882590; Fr. Pat. 373854; J. Soc. Chem. Ind. 1907, 778. **Menthol ether**, *v.* Bibus and Scheubler, Eng. Pat. 8544; U.S. Pat. 830043; J. Soc. Chem. Ind. 1906, 233. **Cinnamylsalicylic acid**, *v.* Wellcome, Jowett and Pyman, Eng. Pat. 7125; Chem. Soc. Proc. 1907, 317; J. Soc. Chem. Ind. 1906, 1002. The **Dithiosalicylic acids** are used as substitutes for iodoform. Their sodium salts, known as *Dithion*, are antiseptics, and are used in the treatment of rheumatic fever and of foot-and-mouth disease (Cassella & Co., D. R. P. 189200; Chem. Soc. Abstr. 1908, i. 177; Farb. v. Heyden, Eng. Pats. 13027, 14443, 5263; D. R. PP. 51710, 64347; Frdl. ii. 141; iii. 840; J. Soc. Chem. Ind. 1890, 213, 821; 1892, 369; Baum, D. R. PP. 46413, 71425; Frdl. ii. 140; iii. 841). The basic bismuth salt, under the name of *Thioform*, is used to treat diseases of the eye, ear, and nose, and in veterinary surgery as a substitute for iodoform in eczema, erysipelas, &c. Of the halogenated salicylic acids, the iodo acids find application in medicine. **2-5-Diodosalicylic acid** (Lautemann, Annalen, 120, 304) is used as an analgesic, antithermic, and antiseptic compound. The methyl ester, *Sanoform*, is used as a desiccant for wounds and ulcers and as a substitute for iodoform. **Monoiodo acids**, *v.* Hasse, D. R. P. 224536; Chem. Soc. Abstr. 1910, i. 740.

$\beta\beta$ -Trichloro-tert-butyl salicylate, prepared by

the action of acetone chloroform and salicyl chloride has m.p. 81° – 82° , b.p. 170° . *Tribromo-tert-butyl salicylate* has m.p. 90° – 91° . *Trichloro-iso-propyl salicylate* is an oily liquid. These compounds have analgesic properties and can be used internally (Wolffenstein, D. R. P. 267381).

Salicylsulphonic acid $C_6H_3OH(SO_3H)COOH$ (Remsen, Annalen, 179, 107), also known as *sulphosalicylic acid*, is used in the treatment of articular rheumatism. It is also a delicate reagent for albumin and a precipitant for all kinds of proteids in urine (Roch, Pharm. Centr. 1889, 30, 549). With dilute ferric chloride solution it gives a Bordeaux red tint, not destroyed by hydrochloric acid. Methylglyoxal gives no colour. Millon's reagent gives a red colour. The sodium salt is used as a substitute for salol. By successive nitration and bromination of this acid, the colouring matters known as *salicylic orange* and *salicylic yellow* are obtained. The former is said to dye wool and silk dark yellow or orange, the latter yellow (Chem. Fab. auf Actien vorm. E. Schering, D. R. PP. 15117, of 1880; 15889 of 1881).

5-Nitrosalicylic acid $C_6H_3(OH)(NO_2)COOH$. Prepared by nitrating salicylic acid with a mixture of sulphuric and nitric acids; m.p. 230° . **5-Aminosalicylic acid** $C_6H_3(OH)(NH_2)COOH$. Prepared by the reduction of the above nitro-compound (D. R. P. 77806; Frdl. iv. 54; Fischer and Schaar-Rosenberg, Ber. 1899, 82). Used in the treatment of articular rheumatism and in the production of azo-dyestuffs (Bayer & Co., D. R. PP. 51504, 58271, 60494, 60500, 62133, 62134, 75293, 86314; Frdl. ii. 325; iii. 610, 612, 614 *et seq.*, 632; iv. 795; Kalle & Co., D. R. P. 11640; Chem. Zentr. 1901, i. 152; Meldola, Foster and Brightman, Chem. Soc. Trans. 1917, iii. 536); oxazine dyestuffs (Bad. Anil. u. Sod. Farb. D. R. P. 78710; Frdl. iv. 484); and sulphurised dyestuffs (Höchst, Farb., D. R. P. 118440, 118702).

Acetylsalicylic acid $C_6H_4(OCOCH_3)COOH$ (*Aspirin*). Prepared by treating salicylic acid or sodium salicylate with acetyl chloride (Kraut, Annalen, 150, 11; Erdmann, Ber. 1899, 3572; *v.* also F. Bayer & Co., Eng. Pats. 27088, 9123; J. Soc. Chem. Ind. 1899, 1154; 1900, 373; Krannichfeldts, Ber. 1914, 47, 156, m.p. 131.5° – 132.5° (corr.)). Used instead of the salicylates, as being insoluble in the gastric juice, it is devoid of irritating effects on the stomach. For salts of acetylsalicylic acid, *see* Bouvet (Bull. Sci. Pharm. 1917, 24, 86). *Sodium acetylsalicylate* (hydro-pyrine); *lithium acetylsalicylate* (apyrone, grifa); *calcium acetylsalicylate* (soluble aspirin, kalmopyrine, solupyrine) are used in medicine. It is claimed for the calcium salt that it does not cause pharyngeal or gastric pain like the free acid, and that it occasions less renal irritation, whilst it has all the therapeutic properties of acetylsalicylic acid. **Acetylsalicylic acid chloride** may be obtained by the action of phosphorus pentachloride on acetylsalicylic acid in presence of dimethylaniline (D. R. PP. 201325, 201326), or by heating the acid with thionyl chloride in benzene (D. R. P. 277659 (1911)). On the condensation of acetylsalicyl chloride with sodio-ethyl malonate and sodio-ethyl cyanacetate, and the consequent formation of derivatives of the benzstetronic acid group, *see* R. Anschütz, Ann. 1909, 367, 169. **Salicyloacetic acid**, *v.*

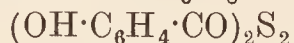
Meister, Lucius and Bruning, Eng. Pat. 12179; J. Soc. Chem. Ind. 1898, 487. **Acetamidoethyl-salicylic acid** $C_6H_3(OC_2H_5)(NH\cdot COCH_3)COOH$ (*Benzacetin*), v. Kuchler and Buff, D. R. P. 71258; Frdl. iii. 88. Used in the treatment of neuralgia.

5-Iodosalicylic acid $OH\cdot C_6H_3I\cdot CO_2H$ is prepared by treating the hydrochloride of 5-amino-salicylic acid with sulphuric acid, diazotising, and adding hydriodic acid. It forms white needles, m.p. 198° ; the *acetyl* derivative crystallises in needles, m.p. 166° ; the ethyl ester (*cf.* Schmitt, Zeitsch. für Chemie, 1864, 322), prepared by boiling the acid with absolute alcohol containing 15 p.c. of sulphuric acid, forms long, colourless needles of aromatic odour, m.p. 70° – 71° . The isomeride **3-iodosalicylic acid**



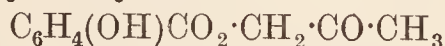
prepared similarly from the sulphate of the corresponding amino-acid, crystallises in needles, m.p. 199° , yields an *acetyl* derivative, white plates, m.p. 135° , and an *ethyl ester* which is obtained as a colourless oil. The two acids on addition of iodine yield the same 3:5-diiodo-salicylic acid $OH\cdot C_6H_2I_2\cdot CO_2H$, white needles, m.p. 228° , *acetyl* derivative, hard, white plates, m.p. 153° (Brenans and Prost, Compt. rend. 1923, 176, 1626–1629; J. Chem. Soc. Abstr. 1923, 123, 124, i. 797). According to P. Brenans and C. Prost (Compt. rend. 1924, 178, 1010) **4-iodosalicylic acid** in colourless needles, turning brown at 200° , m.p. 228° (decomp.), is prepared from 4-nitro-*o*-toluidine by acetylation, oxidation to 4-nitroacetylanthranilic acid, deacetylation, and diazotisation to 4-nitrosalicylic acid, the ethyl ester of which was reduced; from the diazonium sulphate of the resulting amino compound hydriodic acid yields *ethyl 4-iodosalicylate* (needles, m.p. 21°), which was hydrolysed. The *acetyl* derivative of the acid forms colourless crystals, m.p. 156° (Chem. Soc. Abstr. 1924, 126, i. 641).

Thiolsalicylic acid $OH\cdot C_6H_4\cdot CO\cdot SH$ may be prepared by allowing an alcoholic solution of an alkali hydrosulphide to act on salicyloyl chloride or acylsalicyloyl chloride. It forms white crystals, m.p. 33° , with an odour like phosphorus. With ferric chloride it gives a reddish-violet coloration, which disappears with precipitation of **salicyloyl disulphide**



m.p. 129° . The alkali and alkaline-earth salts readily decompose it, giving sulphur and hydrogen sulphide (Chemische Fabrik von Friedrich Heyden, D. R. P. 365212, from Chem. Zentr. 1923, ii. 251–252; J. Chem. Soc. Abstr. 1923, 123, 124, i. 797).

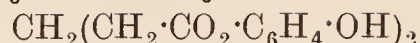
Acetonyl salicylate



(*Salacetol* or *Salantol*) (van Eck, *l.c.*; Fritsch, D. R. P. 70054; Frdl. iii. 839; Eng. Pat. 3961; J. Soc. Chem. Ind. 1894, 274) is used as a substitute for salol in the treatment of rheumatism, neuralgia, and influenza. For estimation, v. Eckenroth and Koch, Pharm. Zeit. 1893, 38, 593; Helbing and Passmore, *ibid.* 621.

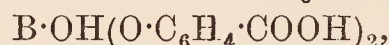
Monoglycol ester $C_6H_4(OH)CO\cdot O\cdot CH_2\cdot CH_2OH$ (*Spirosal*) (Bayer and Co., Eng. Pat. 4055; J. Soc. Chem. Ind. 1905, 1030; Impens, Pflüger's Archiv. 1907, 120, 1). Used in the treatment of rheumatism.

Trimethylene disalicylate



is prepared by the esterification of the glycol with twice its weight of salicylic acid in presence of half its weight of concentrated sulphuric acid at a temperature not exceeding 100° . The ester which solidifies on cooling is colourless and odourless, m.p. 77° . Has antirheumatic properties (Glover, U.S. Pat. 1286944).

Phenyl and naphthyl ethers $RO\cdot C_6H_4\cdot COOH$ (v. Akt. Ges. f. Anifabr., Fr. Pat. 347734; J. Soc. Chem. Ind. 1905, 346). **Methyl and ethyl salicylglycollates** (v. Soc. Chem. Ind. Basle, Eng. Pat. 24672; J. Soc. Chem. Ind. 1905, 902). **Indoform** is the trade name given to a mixture of salicylic acid, acetylsalicylic acid, and methyl-salicylate (Frerichs, Apoth. Zeit. 1908, 23, 641). The condensation product of **gallic and salicylic acids** $OH\cdot C_6H_4\cdot CO\cdot O\cdot CO\cdot C_6H_2(OH)_3$, known as *Salitannol*, is used as an antiseptic and a substitute for salol (F. Bayer & Co., Eng. Pat. 9898; J. Soc. Chem. Ind. 1898, 487). The condensation product of **boric and salicylic acids**



Borosalicylic acid, and its sodium salt, known as *Borsalyl* or *Borosalyl*, are used as antiseptics. A mixture of hydrogen peroxide, boric acid, and salicylic acid, known as *Aseptin*, is used for the same purpose. Condensation product with *epi*- and *dichlorhydrins* (v. Lange, D. R. P. 184382; Chem. Soc. Abstr. 1907, i. 930).

Salicylonitrile $C_6H_4(OH)CN$. Prepared by treating salicaldoxime with acetic anhydride and subsequent hydrolysis (Tiemann, Ber. 1887, 3083; Spilker, *ibid.* 1889, 2771; Bone, Chem. Soc. Trans. 1893, 1350); m.p. 98° . Polymeride of saliconitrile (v. Miller, Ber. 1889, 2790).

Salicylamide $C_6H_4(OH)CONH_2$. Prepared by treating methyl or ethyl salicylates with concentrated aqueous ammonia at 100° (Spilker, Ber. 1889, 2767; Limpricht, Annalen, 98, 258; McCoy, Amer. Chem. J. 21, 116); m.p. 139.9° (corr.) (Remsen and Reid, *ibid.* 413); used in medicine as a substitute for salicylates. Labile isomerism among the benzoyl derivatives of salicylamide (v. Titherley and Hicks, Chem. Soc. Trans. 1905, 1207; Titherley, Chem. Soc. Proc. 1905, 288; McConnan and Titherley, Chem. Soc. Trans. 1905, 1314; Auwers, Ber. 1905, 38, 3256; 1907, 40, 3506; Einhorn and Schupp, *ibid.* 1905, 38, 2792; Einhorn and Haas, *ibid.* 3627).

Anhydrides of salicylic acid.

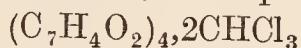
Salicylosalicylic acid $O[C_6H_4\cdot COOH]_2$. Prepared by condensing salicylic acid or its salts with phosphorus trichloride or oxychloride, thionyl chloride, &c. (Gerhardt, Annalen, 87, 159; Marker, *ibid.* 124, 249; Kraut, *ibid.* 150, 13; Boehringer and Sons, Eng. Pat. 11457; U.S. Pat. 922995; D. R. PP. 211403, 214044, 220491; J. Soc. Chem. Ind. 1909, 382, 1104; 1910, 649), m.p. 147° – 148° . Soluble without decomposition in sodium carbonate solution, but decomposed by boiling alkali hydroxide into salicylic acid; does not give a coloration with ferric chloride (Schiff, Annalen, 163, 219). For derivatives, see Schroeter, Ber. 1919, 52, [B.] 2224.

Disalicylide $(C_6H_4CO_2)_2$. Prepared by passing carbonyl chloride into an ice-cold solution of salicylic acid in pyridine (Einhorn and Pfeiffer, Ber.

1901, 34, 2951); m.p. 200°-201°. **Salicylide** or

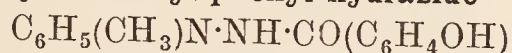
Tetrasalicylide $C_6H_4 \begin{matrix} \diagup CO \cdot O \cdot C_6H_4 \cdot CO \cdot O \\ \diagdown O \cdot CO \cdot C_6H_4 \cdot O \cdot CO \end{matrix} C_6H_4$.

Prepared by dissolving salicylic acid in toluene or xylene and gradually adding phosphorus oxychloride (Anschütz, Ber. 1892, 25, 3506; D. R. PP. 68960, 69708; Frdl. iii. 822, 824); m.p. 261°-262°. There is also formed a polymeride, m.p. 325°, from which it is separated by boiling with chloroform, a compound



being formed. Anschütz (Annalen, 1893, 273, 94) makes use of this in the preparation of pure chloroform.

Salicyl- α -methyl-phenyl-hydrazide



is used in the treatment of neuralgia and rheumatism under the name of *Agathin* and *Cosmin* (Allen, l.c.).

For the antiseptic action of benzoic acid, salicylic acid, cinnamic acid, and their salts, see Waterman and Kuiper (Rec. trav. chim. 1924, 43, 323; Chem. Soc. Abstr. 1924, 126, i. 912).

DETECTION AND ESTIMATION.

A dilute aqueous solution of salicylic acid gives an intense violet coloration with ferric chloride which slowly changes to brownish yellow. The reaction depends on the presence of the ferric ion. It does not occur in presence of sodium phosphate since ferric phosphate is then formed. Free acids, especially hydrochloric and acetic acids, interfere with this reaction. Cf. Langkopf, Chem. Zentr. 1912, i. 444. Phenol and resorcinol also give a violet colour with ferric chloride, but the addition of two drops of lactic acid changes the colour to yellow-green in the case of phenol and resorcinol, whilst the colour produced by salicylic acid remains unchanged (Itallie, Apoth. Zeit. 4, 99). If phenols are present, Freyer (Chem. Zeit. 17, 69) recommends extraction with ether, evaporation to dryness and dissolution of the residue in absolute alcohol. If a violet coloration is produced with ferric chloride, salicylic acid is present as phenols give no coloration in alcoholic solution. A solution of copper sulphate, when added to a solution of salicylic acid or its salts, gives an emerald-green coloration in 2000 parts of water, destroyed by ammonia or acids. Solutions of silver nitrate or lead acetate give white precipitates with neutral salts, but not with the free acid. According to Endemann (J. Soc. Chem. Ind. 1896, 791), if salicylic acid is dissolved in formaldehyde solution, a red solid is precipitated in a magenta-coloured solution. A good test is that known as Millon's reaction (Lintner, Zeitsch. angew. Chem. 1900, 707). The solution is boiled with a few drops of a 10 p.c. solution of acid mercuric nitrate for 2 minutes; 2-3 drops of dilute sulphuric acid are added and then a few drops of a solution of sodium nitrite. A red colour is at once formed in the presence of salicylic acid. Jorissen recommends treating a solution of the acid or its salts with sodium nitrate and a little acetic acid, followed by 2 drops of copper sulphate solution: a blood-red colour is produced on boiling. Cf. Sherman and Gross, J. Ind. Eng. Chem. 1911, 3, 492; Barral, Bull.

Soc. chim. 1912, [iv.] 11, 417; Van Raalte, Chem. Weekblad, 1912, 9, 1004. For other tests, v. Reichard, Pharm. Zentr. H. 1910, 51, 743; Self, Pharm. J. 1915, 94, 521. J. M. Wilkie (J. Soc. Chem. Ind. 1911, 30, 402) recommends adding to an aqueous solution 10 c.c. N/10 sodium carbonate and 10 c.c. N/10 iodine solution, followed after five minutes by the addition of 5 c.c. of 3N sulphuric acid. A precipitate of 2·4·6-tri-iodo-phenol is obtained, and it is claimed that the method can be used for solutions containing as little as 1 part of acid in 870,000.

In the absence of any other acid substance, salicylic acid may be estimated by titration with standard alkali, using phenolphthalein as an indicator (Barthe, Bull. Soc. chim. 1894, 11-12, 516).

Volumetric methods. A known weight of the substance is dissolved in water to which a little sodium hydroxide has been added, and a volume containing about 0·1 gm. salicylic acid is diluted with water to 100 c.c. in a stoppered bottle. 10 c.c. hydrochloric acid, sp.gr. 1·1, are added and then a known volume of a solution of sodium bromide and sodium bromate, about 50-60 c.c., so as to give about 75 p.c. excess of bromine. In another bottle is placed an equal quantity of bromate solution. A 10 p.c. solution of potassium iodide is added to each bottle, and the liberated iodine titrated with N/10 thiosulphate solution. The difference in the volume of thiosulphate solution used in the titrations gives the amount of bromine which has reacted with the salicylic acid (Freyer, Chem. Zeit. 1896, 20, 820; Fresenius and Grünhut, Zeitsch. anal. Chem. 1898, 38, 292; von Generisch, Zeitsch. Nahr. Genussm. 1908, 16, 209; cf. Siedell, J. Amer. Chem. Soc. 1909, 31, 1168; Authenrieth and Beuttel, Arch. Pharm. 1910, 248, 112; Schulz, Bied. Zentr. 1907, 36, 602). Another method consists in precipitating salicylic acid from an alkaline solution with standard iodine solution and titrating back the excess of iodine with thiosulphate (Messinger and Vortmann, Ber. 1890, 23, 2753). Fresenius and Grünhut (l.c.) state that this method is inaccurate, but Messinger (J. pr. Chem. 1900, [iii.] 61, 236) and Bougault (Compt. rend. 1908, 146, 403) have shown that under proper conditions it is quite satisfactory.

Gravimetric method.—When iodine is added to a solution of salicylic acid, a red precipitate is formed which consists of a mixture of the potassium salt of 3:5-diiodosalicylic acid and diphenylene-quinone (Lautemann, Annalen, 1861, 120, 309; Benzinger and Kameron, Ber. 1878, 11, 557). Bougault (l.c.) has devised a method for estimating salicylic acid, which depends on the insolubility of the latter compound. A portion of the substance containing about 0·1 gm. salicylic acid is weighed out and dissolved in a solution containing 1 gm. sodium carbonate in 50 c.c. water. Iodine is added, the solution heated for 20 mins. on the water-bath, and then boiled for 10 mins. under the reflux, iodine being added from time to time to ensure excess being present. The excess of iodine is removed with sodium sulphite, the precipitate collected on a Gooch crucible, dried and weighed. This weight, multiplied by 138/344, gives the amount of salicylic acid

present. For estimation as picric acid, *v. Spica*, Gazz. chim. ital. 1895, 25, i. 207; Montanari, *ibid.* 1904, 34, i. 207.

A colourless solution of salicylaldehyde yields a yellow coloration when treated with a trace of alkali; the colour is destroyed by acids and even by carbon dioxide. The aldehyde may therefore be used as an indicator in the titration of salicylic acid in a solution also containing salicylaldehyde. To determine salicylic acid in an ethereal solution containing both substances, the solution is extracted several times with N/20 sodium bicarbonate solution and then with water; the last aqueous extract must give a yellow colour with a drop of alkali solution. If this is not the case, all the acid has not been removed and the extraction must be repeated. The united extracts are titrated with N/20 sulphuric acid; this is added in small quantities at a time and the solution boiled to expel carbon dioxide. The final disappearance of the yellow colour denotes the end point of the titration (Berg. Chem. Zeit. 1919, 43, 129; J. Soc. Chem. Ind. 1919, 337 A).

Colorimetric method (v. Estimation in wines).

Detection and estimation in wines.—The methods differ chiefly in the solvent used to extract the salicylic acid. Ether was used at first, but it was found that it extracted another substance which coloured ferric chloride solution violet; probably the maltol of Brandt (Pereira, Bull. Soc. chim. 1901, [iii.] 25, 475; Wiegert, Chem. Zentr. 1888, 1511; Medicus, *ibid.* 1890, ii. 28; Spica, Gazz. chim. ital. 1895, 25, i. 207). The following solvents have been recommended: ether and light petroleum (Abraham, J. Pharm. Chim. 1898, [vi.] 8, 410; da Silva, Compt. rend. 131, 423; Ann. Chim. anal. 6, 11; Bull. Soc. chim. 1901, [iii.] 25, 726; Conrad, Apoth. Zeit. 1900, 15, 412; Pellet, Bull. de l'Assoc. Chim. Sucr. 1900, 18, 305; Ann. Chim. anal. 5, 418; 6, 364; Saporetti, Boll. chim. farm. 1908, 47, 751); chloroform (Weigert, *l.c.*; von der Heide and Jakob, Zeitsch. Nahr. Genussm. 1910, 19, 137); carbon tetrachloride (Bigelow, J. Soc. Chem. Ind. 1909, 1158); benzene (Lindeman and Motteu, Bull. Soc. chim. [iii.] 8, 441); and toluene (Bigelow, *l.c.*; Vitali, Boll. chim. farm. 1910, 45, 701; Cattini, *ibid.* 641). Harvey (Analyst, 1903, 28, 2) recommends the use of a 1 p.c. solution of iron alum, and proceeds as follows: 100 c.c. of wine are made acid with dilute sulphuric acid, and the salicylic acid extracted twice with ether. The ethereal solution is shaken out twice with water containing a known amount of N/2 or N/10 alkali. The solution is neutralised and made up to 250 c.c. 50 c.c. are taken and the intensity of colour obtained on the addition of ferric chloride compared with that in standard tubes containing a known amount of salicylic acid (*cf.* Pellet and de Grobert, Bull. de l'Assoc. Sucr. Dist. 1902, 20, 289; Cassal, Chem. News, 1910, 101, 289). *In fruit juices.* Heintz and Limbrich, Zeitsch. Untersuch. Nahr. Genussm. 1913, 25, 706; Analyst, 1913, 420. *In beer.* Pinette (Chem. Zeit. 14, 1570; J. Soc. Chem. Ind. 1891, 165), Abraham (*l.c.*), Elion (Rec. trav. chim. 7, 211), Horn (*ibid.* 341), and Snyders (Chem. Zentr. 1888, 1186) use the ferric chloride method, whilst Schoepp (7th ed. Tydschr. Pharm. 7, 67; La Biere,

4, 182) prefers Millon's reagent (*v. supra*). *In milk* (Saporetti, *l.c.*; Revis and Payne, Analyst, 1907, 32, 286; Süss, Pharm. Centr. 41, 437; Breustedt, Arch. Pharm. 1899, 237, 170; Philippe, Chem. Zentr. 1912, i. 288). *In foods.* 50 grms. of the crushed substance are placed in a 300 c.c. flask, a little water added, then 15–20 c.c. of a saturated solution of basic lead acetate, followed by 25 c.c. of sodium hydroxide to render the solution alkaline. 15–20 c.c. of N/1 hydrochloric acid are added and the mixture made up to 300 c.c. The hydrochloric acid dissolves the lead salicylate, leaving the lead tannate insoluble. Then colorimetrically with ferric chloride (Harry and Mummery, Analyst, 1905, 30, 124; von Fellenberg, Zeitsch. Nahr. Genussm. 1910, 20, 63; *cf.* Gorni, Rec. intern. Falsif, 1906, 19, 16; Boll. chim. farm. 44, 409; Dubois, J. Amer. Chem. Soc. 1906, 36, 602; Sherman, J. Ind. Eng. Chem. 1910, 2, 24; Taffe, Bull. Soc. chim. 1902, [iii.] 27, 701; Ann. Chim. anal. 1902, 7, 18; 1903, 8, 24; McElroy, J. Amer. Chem. Soc. 1894, 16, 198). *In urine*, *v. Petermann*, Ann. Chim. anal. 1901, 6, 4.

For the detection of salicylic acid in wine, fruit syrup, and the like, 5 c.c. is shaken gently for half a minute with 6 c.c. of chloroform, and the lower layer is separated and filtered through paper to remove suspended aqueous particles. The clear liquid is vigorously shaken with 1 c.c. of water and the mixture again poured through the same filter into a test tube; 0.5 c.c. of a solution, containing 1 drop of 10 p.c. ferric chloride solution in 20 c.c. of water, is added and the mixture shaken. The presence of 1 mg. of salicylic acid per 100 c.c. of wine or syrup is indicated by a strong violet-blue colour in the water layer.

ISOMERIDES OF SALICYLIC ACID.

***m*-Hydroxybenzoic acid** $C_6H_4(OH)COOH$. Prepared by the action of nitrous acid on *m*-aminobenzoic acid (Gerland, Annalen, 91, 189), and by fusing *m*-benzenesulphonic acid (Barth, *ibid.* 148, 33; Graebe, *ibid.* 280, 67), *m*-chlorobenzoic acid (Remsen, Zeitsch. Chem. 1871, 81, 199; Dembey, Annalen, 148, 222), *m*-cresol (Barth, *ibid.* 154, 361), or benzoic acid (Barth and Schreder, Monatsh. 3, 802) with sodium hydroxide. Crystallises in microscopical laminae, m.p. 188° (Kellas, Zeitsch. physikal. Chem. 24, 221), 200° (Fischer, Annalen, 127, 48). Gives no coloration with ferric chloride. Can be distilled unchanged; reduction with sodium amalgam yields *m*-hydroxybenzyl alcohol. By heating with 90 p.c. sulphuric acid at 210°, *m*-benzodihydroxyanthraquinone, anthraflavic acid, and anthrarufin are produced; with sulphuric acid in the presence of boric acid, hexahydroxyanthraquinone is the product (Bayer & Co., D. R. P. 81959; Frdl. iv. 273).

***p*-Hydroxybenzoic acid** $C_6H_4(OH)COOH$. Occurs in the pods of *Catalpa bignonioides* (Walt). Prepared by the action of nitrous acid on *p*-aminobenzoic acid (G. Fischer, Annalen, 127, 145), and by fusing various gums (*e.g.* benzoin, dragon's blood) (Barth and Hlasiwetz, *ibid.* 134, 274; 139, 78), carthamin (Malin, *ibid.* 136, 117), tyrosin (Barth, *ibid.*

136, 112), phloretic acid (Barth, *ibid.* 152, 96), *p*-cresol (Barth, *ibid.* 154, 359), *p*-benzene sulphonic acid (Remsen, *ibid.* 178, 281), or benzoic acid (Barth, *ibid.* 164, 141; Barth and Schreder, *Monatsh.* 3, 802) with potassium hydroxide. It can also be prepared by heating potassium salicylate under pressure at 180° (v. Heyden, *Nachf. D. R. P.* 48356; *Frdl.* ii. 132); by heating potassium phenate and carbon dioxide at 220° (v. Kolbe's process, *supra*); together with salicylic acid by boiling an alkaline solution of phenol with carbon tetrachloride (Reimer and Tiemann, *Ber.* 1876, 1285; v. *supra*); and as the ethyl ester by the hydrolysis of apigenin diethyl ether (Perkin, *Chem. Soc. Trans.* 1897, 815). Monoclinic prisms containing 1 mol. of water of crystallisation (Negri, *Gazz. Chim. ital.* 26, i. 65). For solubility, v. Walker and Wood, *Chem. Soc. Trans.* 1898, 622. Gives a yellow amorphous precipitate with ferric chloride. Distillation of the calcium salt yields phenol, salicylic acid, hydroxyisophthalic acid, and carbon dioxide (Goldschmiedt and Herzog, *Monatsh.* 3, 132).

The only derivatives of medicinal importance are the following: Methyl *p*-amino-*m*-hydroxybenzoate, *orthoform*, used as an antiseptic and local anæsthetic; the sodium salt of methyl *p*-amino-*m*-hydroxybenzene sulphonate, *sulphonated orthoform*, and methyl *m*-amino-*p*-hydroxybenzoate, *orthoform new*, both of which are used as substitutes for *orthoform* (Einhorn, *D. R. PP.* 97334, 97335; *Annalen*, 311, 26; *Ber.* 1897, 991). They cannot be used for subcutaneous injections as they have an acid reaction. The glycocoll derivatives are found to have a neutral reaction and have been used as anæsthetics (Einhorn and Oppenheimer, *Annalen*, 311, 154; *D. R. P.* 106502).

SALIFORMIN v. SYNTHETIC DRUGS.

SALINAPHTHOL v. SALICYLIC ACID.

SALINIGRIN v. GLUCOSIDES.

SALIT v. SALICYLIC ACID and SYNTHETIC DRUGS.

SALITANNOL v. SALICYLIC ACID.

SALMON OIL. This oil is obtained on a very large scale from the salmon (*Salmo salar*, Linn.), as a by-product in the salmon-preserving industry of British Columbia. The fish contains about 20 p.c. of oil. The oil is pale golden-yellow, has a mild smell, and a tolerably pleasant taste. For the characteristics, see OILS, FIXED, AND FATS.

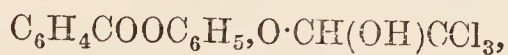
The oil is imported in large quantities into this country, and is used in the leather and soap industries. J. L.

SALMON RED v. PRIMULINE AND ITS DERIVATIVES.

SALOCHININ, SALOCOLL, SALOCRESOL, SALOPHEN, v. SYNTHETIC DRUGS.

SALOL v. SALICYLIC ACID.

SALOL-CHLORAL. An oily liquid



obtained by heating salol with chloral hydrate.

SALOL-RED $\text{C}_{19}\text{H}_{16}\text{O}_4$, a reddish-brown powder, m.p. 116°–119°, obtained by heating salicyl metaphosphoric acid with phenol at 150°. Soluble in alkalis. Dyes wool directly (Langer, *Apoth. Zeit.* 1921, 36, 42; Zimmermann, *ibid.* 36, 17).

SALOPHEN. Trade name for acetylamino-

phenyl salicylate. *p*-Nitrophenyl salicylate dissolved in glacial acetic acid is mixed with zinc-dust and anhydrous acetic acid, and heated under a reflux condenser, cooled and poured into water. M.p. 187° (Brewster, *J. Amer. Chem. Soc.* 1918, 40, 1136). See SALICYLIC ACID.

SALSEPARIN v. SARSAPARILLA.

SALT, COMMON, v. *Sodium chloride*, art. SODIUM; v. HALITE.

SALT, EPSOM. *Crystallised magnesium sulphate*.

SALT, FUSIBLE. *Sodium ammonium phosphate*.

SALT, GLAUBER'S. *Sodium sulphate*.

SALT, GLAZIER'S. *Potassium sulphate*.

SALT, MICROCOSMIC. *Sodium ammonium phosphate*.

SALT OF AMBER. *Succinic acid*.

SALT OF LEMERY. *Potassium sulphate*.

SALT OF LEMONS v. OXALIC ACID.

SALT OF SATURN. *Lead acetate*.

SALT OF SODA. *Sodium carbonate*.

SALT OF SORREL v. OXALIC ACID.

SALT OF TARTAR. *Potassium carbonate*.

SALT OF TIN. *Stannous chloride*.

SALT OF VITRIOL. *Zinc sulphate*.

SALT PERLATE. *Sodium phosphate*.

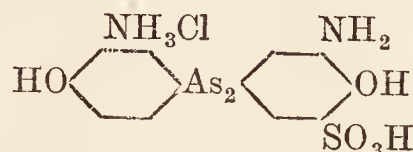
SALTPETRE. *Nitre*; *potassium nitrate*.

SALT, SEDATIVE. *Boric acid*.

SALUFER. Trade name for sodium silicofluoride.

SALUMIN v. SALICYLIC ACID and SYNTHETIC DRUGS.

SALVARSAN v. ARSENICALS, ORGANIC; SYNTHETIC DRUGS. The sulphur-containing constituent of salvarsan prepared by the hypsulphite reduction method is 3:3'-diamino-4:4'-dihydroxy-5-sulphoarsenobenzene monohydrochloride



(King, *Chem. Soc. Trans.* 1921, 119, 1107, 1415).

For the viscosity and toxicity of salvarsan solutions, see Voegtlin, Johnson and Dyer (*U.S. Public Health Rep.* 1924, 179; *Chem. Soc. Abstr.* 1924, 126, i. 911).

SALVIA SEEDS, OIL FROM. According to R. Br. M. G. Rau and J. L. Simonsen (*Indian Forest Records*, 1924, 10, 23), the ground seeds of *salvia plebeia* on extraction with cold benzene gave 11 p.c. of an oil having the following characters: d_{20}^{30} 0.934, n_D^{30} 1.4832, acid value 6.0, saponification value 195.0, unsaponifiable matter 0.02 p.c., acetyl value nil, iodine value 131.1, Reichert Meissl value 1.3, solidification point of the insoluble fatty acids 10.5°–11°. Stearic acid was the only saturated acid present. Linolenic acid, linolic acid, and oleic acid were identified in the oil (*Chem. Soc. Abstr.* 1924, 126, i. 609).

SALVIANIN, SALVIN, SALVININ v. ANTHOCYANINS.

SALVIOL v. CAMPHORS.

SALZBURG VITRIOL v. COPPER SULPHATE.

SAMANDARINE $\text{C}_{26}\text{H}_{40}\text{ON}_2$ and *Samandarine* $\text{C}_{22}\text{H}_{31}\text{ON}$ are two alkaloids from the skin of the newt, *Salamandra maculosa*, and were isolated as crystalline sulphates by Faust (*Arch. exp. Path. Pharm.* 1898, 41, 229; 1899,

43, 84). They are powerful nerve poisons. The latter may be an isoquinoline derivative.

G. B.

SAMARIUM. Sym. Sa. At.wt. 150.43 (Stewart and James, Owens, Balke and Kremers). In 1879 Lecoq de Boisbaudran isolated from samarskite the oxide *samaria* (v. CERIUM EARTHS, and Compt. rend. 88, 322; 89, 212), which was subsequently recognised by Brauner as occurring in the 'didymium' earth of cerite (Chem. Soc. Trans. 1883, 43, 278). The oxide obtained from samarskite by Delafontaine, to the metallic constituent of which the name '*decipium*' was given, consists partly of samaria (Compt. rend. 1878, 87, 632; cf. Marignac, *ibid.* 1880, 90, 899).

Occurrence.—Samarskite, cerite, orthite, ytterbite, monazite. According to Tamaka (Chem. Soc. Abstr. 1924, ii. 467), samarium is the active agent in the cathodo-luminescence of most samples of fluor-spar. Other rare earths and also thallium are occasionally active.

Separation and purification. Samarium was first separated by the fractionation of its double potassium sulphate, the solubility of which in aqueous alkali sulphate is greater than that of the neodymium and praseodymium double sulphates, but less than that of the corresponding salts of the terbium metals. The separation from the neodymium and praseodymium fraction can be effected by fractional precipitation with ammonia and from the terbium metals by crystallisation of the double sulphates (Cleve, Compt. rend. 1883, 97, 84; Bull. Soc. chim. 1885, [ii.] 43, 53). The neodymium and praseodymium can also be partially removed by fractional decomposition of the nitrates and the separation completed by crystallisation of the double sulphates (Bettendorf, Annalen, 1891, 263, 164). In these operations samaria shows itself to be a weaker base than neodymia or praseodymia, the element, samarium, occupying in the rare earth series a position between neodymium and the terbium metals as indicated by the solubilities of its salts and the basic strength of its oxide.

The most soluble portions of the double nitrate fractionations for neodymium and praseodymium, according to the methods of von Welsbach, Demarçay and Drossbach, may, therefore, be taken as a convenient starting material for the separation of samarium, and the double magnesium nitrate crystallisation in nitric acid (sp.gr. 1.3) affords a means of separating completely samarium from neodymium, the latter element having the less soluble double salt (Demarçay, Compt. rend. 1896, 122, 728). The more soluble double nitrates of europium and gadolinium are also eliminated by a prolonged application of this method (Compt. rend. 1900, 130, 1019, 1185; cf. Muthmann and Weiss, Annalen, 1904, 331, 1). A combination of crystallisation methods with simple nitrates and double magnesium nitrates has been employed in the separation of samarium and neodymium (Feit and Przibylla, Zeitsch. anorg. Chem. 1905, 43, 203).

The purification of the samarium double salt is facilitated by the addition of magnesium bismuth nitrate, which in the subsequent fractionation effects a separation between the double salts of samarium and europium (Urbain and Lacombe, Compt. rend. 1903, 137, 794;

1904, 138, 84, 1166; cf. Eberhard, Zeitsch. anorg. Chem. 1905, 45, 374; Owens, Balke and Kremers, J. Amer. Chem. Soc. 1920, 42, 515).

Metallic samarium, m.p. 1300°–1400°, sp.gr. 7.8, the hardest metal of the cerium group, is a yellow substance prepared by the electrolysis of the anhydrous chloride; it rapidly becomes tarnished with a layer of yellowish oxide.

Samarium carbide SaC_2 . A yellowish crystalline mass, sp.gr. 5.86, produced by reducing samaria with carbon in the electric furnace (900 ampères, 45 volts), is decomposed by water, evolving hydrogen, acetylene, olefines, and paraffins (Moissan, Compt. rend. 1900, 131, 924).

Samarium sulphide Sa_2S_3 , yellow mass, sp.gr. 3.7, is obtained by passing sulphur vapour over the carbide (Annalen, 1908, 361, 190).

Samarium oxide (*Samaria*) Sa_2O_3 , sp.gr. 8.347, is white with a yellowish tinge like the samarium salts of colourless acid radicles. The hydroxide is a gelatinous precipitate. A hydrated peroxide $\text{Sa}_4\text{O}_9 \cdot x\text{H}_2\text{O}$ is produced by precipitating with ammonia in presence of hydrogen peroxide.

Samarium chloride SaCl_3 , prepared by methods generally applicable to the anhydrous chlorides of rare earth metals (v. CERIUM, LANTHANUM, &c.) is a yellowish-white powder, sp.gr. 4.465, melting at 686° to a dark brown liquid. The dry salt absorbs ammonia forming a series of additive compounds, with 1, 2, 3, 4, 5, 8, 9.5, and 11.5 NH_3 (Compt. rend. 1905, 140, 141).

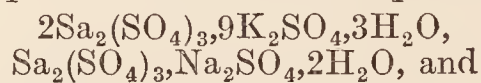
The **hydrate** $\text{SaCl}_3 \cdot 6\text{H}_2\text{O}$, sp.gr. 2.382, crystallises in yellow plates, the **platini-** and **auri-chlorides** are $\text{SaCl}_3 \cdot \text{PtCl}_4 \cdot 10.5\text{H}_2\text{O}$ and



respectively (Cleve, Bull. Soc. chim. 1885, [ii.] 43, 53; Chem. News, 1886, 53, 30, 45, 67, 80, 91, 100; these memoirs contain descriptions of many other samarium salts).

Samarium dichloride SaCl_2 , a dark brown crystalline mass, sp.gr. 3.687/22°, insoluble in alcohol, but decomposed by water yielding samaria, samarium oxychloride, and hydrogen, is of interest as being the only chloride of the rare earth series in which the metal is apparently bivalent; it is produced by reducing the anhydrous trichloride at high temperatures with hydrogen, ammonia, or aluminium powder. Samarium triiodide can be similarly reduced to the diiodide (Matignon and Cazes, Compt. rend. 1906, 142, 83).

Samarium sulphate $\text{Sa}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$, sp.gr. 2.930/18°, forms light yellow crystals more sparingly soluble than neodymium and praseodymium sulphates. The double sulphates,



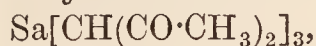
$\text{Sa}_2(\text{SO}_4)_3 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 8\text{H}_2\text{O}$, are more soluble in aqueous alkali sulphates than the corresponding neodymium and praseodymium double salts (Ann. Chim. 1880, [v.] 20, 535; Compt. rend. 1881, 93, 63; Keyes and James, J. Amer. Chem. Soc. 1914, 36, 634).

Samarium carbonate $\text{Sa}_2(\text{CO}_3)_3 \cdot 3\text{H}_2\text{O}$, acicular crystals, obtained by treating with carbonic acid the hydroxide precipitated by ammonia. Alkali carbonates added to soluble samarium salts

produce voluminous precipitates of the double alkali carbonates

$\text{Sa}_2(\text{CO}_3)_3, \text{R}_2\text{CO}_2, x\text{H}_2\text{O}, [\text{R}=\text{Na}, \text{K} \text{ or } \text{NH}_4]$
which gradually become crystalline.

Samarium acetylacetone



m.p. 146° – 147° , prepared by the interaction of samarium nitrate, acetylacetone, and ammonia in aqueous solution, is somewhat more soluble in water than other acetylacetones of the rare earth series; its molecular weight in carbon disulphide solution is double that indicated by the foregoing formula (Biltz, *Annalen*, 1904, 331, 334).

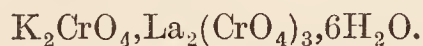
Samarium dimethyl phosphate, cream-coloured, hexagonal prisms, solubility 35.2 at 25° and about 10.8 at 95° .

For other salts see James, Hoben, and Robinson, *J. Amer. Chem. Soc.* 1912, 34, 276; Morgan and James, *ibid.* 1914, 36, 10.

Absorption spectrum.—Samarium salts exhibit a series of absorption bands ranging from $\lambda 559$ to $\lambda 362$, but concentrated solutions must be employed as the intensity of this spectrum is much less than that of neodymium or praseodymium (Demarçay, *Compt. rend.* 1900, 130, 1185).

Spark spectrum not very characteristic (Exner and Haschek, *Sitzungsber. Wien.* 1898, IIc. 108, 1106, 110, 504; Demarçay, *Compt. rend.* 1900, 131, 995). *Reversal spectrum* and *cathode luminescence* (Demarçay, *ibid.* 1900, 130, 1185). *Arc spectrum* (Exner and Haschek, *Die Wellenlängen der Bogenspektren*, 1904).

Lanthanum, praseodymium, neodymium, and samarium form an isomorphous, yellow, difficultly soluble series of chromates of the general formula $\text{M}'''_2(\text{CrO}_4)_3, 8\text{H}_2\text{O}$. The variation in their solubilities shows their importance in processes of fractional precipitation with potassium chromate. The tendency to form sparingly soluble double chromates is marked in the cases of lanthanum, praseodymium, and samarium. Lanthanum forms the salt



The addition of potassium chromate to aqueous salt solutions causes the precipitation in the case of (a) lanthanum, of the simple chromate, if the excess of precipitant is small; (b) praseodymium, of the simple chromate; (c) neodymium, of a mixture of simple and basic chromate; (d) samarium, of an indefinite basic precipitate (H. T. S. Britton, *J. Soc. Chem. Ind.* 1924, 43, 485).

G. T. M.

SAMARSKITE. A complex rare-earth mineral consisting of columbate and tantalate of cerium and yttrium earths with ferrous oxide and 10–13 p.c. of uranium oxide. It breaks with a brilliant, conchoidal fracture, showing a velvet-black colour and pitchy lustre; sp.gr. 5.4–5.8. It is found as orthorhombic crystals embedded in felspar in the Ilmen Mountains, Urals, and in some abundance as masses up to 20 lbs., in the Wiseman and Grassy Creek mica mines in Mitchell Co., North Carolina. Irregular fragments and masses up to 200 lbs. have been found in pegmatite in the Sankara mica mine, Nellore district, Madras (G. H. Tipper, *Rec. Geol. Survey, India*, 1911, 41, 210). Other occurrences are in pegmatite veins at several places in the south of Norway, in Madagascar, and the Caucasus.

L. J. S.

SAMBUNIGRIN v. GLUCOSIDES.

SAMNA or **SAMN**. The Arabic term for 'ghee' or clarified butter, obtained chiefly in Egypt from the milk of the buffalo and in Syria from sheep's and goat's milk; applied also to the fat from the tail of the Barbary sheep (*Ovis tragelaphus*). For analyses see Trimen, *Analyst*, 1913, 242; Droop Richmond, *ibid.* 252.

SAMSONITE. An explosive consisting of nitroglycerin (57–60); nitro-cotton (3–4); potassium nitrate (17–19); wood meal (5–7); ammonium oxalate (12.5–14.5).

The same name has also been applied (Werner and Fraatz, *Centr. Min.*, 1910, 331) to a mineral with the composition $2\text{Ag}_2\text{S}\cdot\text{MnS}\cdot\text{Sb}_2\text{S}_3$, found as small, monoclinic crystals in the Samson mine at St. Andreasberg in the Harz mountains.

L. J. S.

SAMSU. A fermented drink of Eastern Asia made from rice.

SAMUELA CARNEROSANA, a tree related to the yuccas, and growing freely in Mexico; yields seeds from which a light yellow oil may be obtained by extraction with solvents. The oil has the following characters: sp.gr. at 22° 0.9265, iodine value 125.6, acid value 5.13, $n=1.4710$, ester value 187.7. As about 50 p.c. of the dried fruit consists of fermentable sugars (largely lævulose) it might be of value for the production of alcohol (Black and Kelly, *Amer. J. Pharm.* 1922, 94, 477).

SANATOGEN. A preparation consisting of a sodium casein compound of glycerophosphoric acid.

SANATOL. Trade name for a preparation of crude carbolic acid. Used as an antiseptic.

SAND. (*Sable*, Fr.) An accumulation of grains of mineral matter resulting from the disintegration of rocks. It is generally siliceous, since quartz is the most abundant rock-constituent, and by its hardness, lack of cleavage, and chemical stability survives after the associated minerals have disappeared. The microscopic studies of Sorby, Phillips, and others have shown that in some sands a growth of crystalline quartz surrounds the original water-worn grains, the secondary deposit and the nucleus being in crystallographic continuity (*Quart. Journ. Geol. Soc.* 1880, 36, 46; 1881, 37, 21). In sands derived from granitic rocks and crystalline schists, the quartz is often associated with grains of felspar and scales of mica; and A. Dick has pointed out the occurrence in such sands of zircon, rutile, tourmaline, and garnet (*Nature*, 1887, 36, 61). Many other kinds of heavy minerals have been found to be of wide distribution even in the purest quartz sands (T. Crook, *The Systematic Examination of Loose Detrital Sediments*, in F. H. Hatch and R. H. Rastall, *The Petrology of the Sedimentary Rocks*, London, 1913). Many sands are coloured yellow or brown by ferric hydrate, while others are speckled with dark-green grains of glauconite. 'Black sand' usually contains magnetite, ilmenite, chromite, or cassiterite; the titaniferous iron-sand of Taranaki, in New Zealand, and that of the coast of Labrador, have been used as ores. Sands rich in monazite (*q.v.*) supply practically the whole of this mineral used commercially. 'Gem-sands' vary in nature according to the character of the rocks which yielded them, but

frequently contain garnets, spinels, and zircons. By systematically panning and examining the heavy residues or concentrates from river-sands, many useful minerals (gold, platinum, cassiterite, monazite, &c.) may be detected and traced to their sources. 'Volcanic sand' is composed of finely divided lava. Coral-sand and shell-sand consist mainly of fragments of calcium carbonate of organic origin.

Most sands have been deposited as sediments in water, either fresh or salt; but there are also accumulations of wind-drifted materials, known as *Æolian sands*, occurring as dunes along the coast or in the interior of deserts. The quartz grains of desert-sand are usually much more rounded than those of water-borne sand. Blown sand exerts considerable abrasive power, wearing any isolated rocks into characteristic forms. The eroding action of blown sand is taken advantage of in the *sand-blast*, introduced by B. C. Tilghman. By this process, glass and stone may be rapidly engraved or cut by the action of a jet of sand projected with great velocity by means of steam or compressed air. Sand dunes composed of grains of gypsum occur in Arizona and New Mexico, forming deposits of this mineral sufficiently important to be worked commercially.

Fulgurites, or 'lightning-tubes,' are occasionally formed when lightning strikes a sandy soil, the quartz becoming vitrified by the heat, and so forming natural tubes of silica-glass.

Siliceous sand, as free as possible from iron, is valued in the manufacture of glass. Glass-sand is dug near Reigate in Surrey, Lynn in Norfolk, &c., and is largely imported from Fontainebleau in France. Excellent sand occurs at Gweedore in county Donegal. Glass-sand when fused alone gives a clear silica-glass. Sand is also used in the preparation of mortar, concrete, sand-lime bricks, and artificial stone, for which purpose it should be sharp and clean; for polishing and scouring ('silver-sand' and 'Bath bricks'), filtering, and for a variety of purposes.

Sand is largely used as a moulding material for foundry work. The best moulding sand is argillaceous, containing in some cases as much as 6 p.c. of clay. Where a strong adhesive material is required, as for cores in casting, a clayey sand is especially needful. The foundry sand, or loam, is usually prepared by sifting, and may often be advantageously mixed with coke-dust. Facing sand should be coated with carbonaceous matter, such as powdered charcoal or graphite. Sand is also much used in the manufacture of clay-bricks—as a moulding material, for facing, and for mixing with the clay. Another important use is as a refractory material for the manufacture of silica-bricks and furnace linings.

The following analyses are selected from a large number given by Boswell (*l.c.*). A large collection of analyses is also given by Burchard (*l.c.*). I, Glass-sand from Fontainebleau, France (Upper Oligocene age). II, Glass-sand from Godstone, Surrey (Lower Greensand age). III, Glass-sand from Lynn, Norfolk (Lower Greensand). IV, Glass-sand from Huttons Ambo, near Malton, Yorkshire (Lower Oolites). V, Brown sand, used for making black bottles, from Lynn, Norfolk (also alkalis 0·38). VI, Red

moulding-sand from Belfast (Bunter, Triassic age; also TiO_2 0·35, K_2O 2·78, Na_2O 1·50).

	I.	II.	III.	IV.	V.	VI.
SiO_2	99·80	99·56	99·23	99·04	86·28	81·47
Al_2O_3	0·13	0·26	0·59	0·84	1·12	8·84
Fe_2O_3	0·006	0·06	0·04	0·03	3·52	1·84
CaO	trace	—	0·11	0·10	0·45	0·86
MgO	—	—	0·02	0·18	—	0·81
H_2O	0·18	0·24	0·25	0·19	8·25	2·24
	100·116	100·12	100·24	100·38	100·00	100·69

References.—E. F. Burchard, *Min. Res. U.S. Geol. Survey*, 1912 (for 1911), 2, 622. A. B. Searle, *British Clays, Shales, and Sands*, London, 1912. *Special Reports on the Mineral Resources of Great Britain*, *Mem. Geol. Survey*, vol. 6, *Refractory Materials*, 1918. P. G. H. Boswell, *British Resources of Sands suitable for Glass-making, &c.*, London, 1916; supplementary memoir, 1917; 2nd edit. 1918. P. G. H. Boswell, *British Resources of Refractory Sands for Furnace and Foundry Purposes*, London, 1918. L. J. S.

SANDAL, SANDEL, or SANTAL WOOD *v.* SANDERSWOOD.

SANDALWOOD CAMPHOR *v.* CAMPHORS.

SANDARAC, SANDARACIN *v.* RESINS.

SANDERSWOOD. This dyestuff, known also as *Red Sanderswood*, *Santalwood*, or *Sandelwood*, is the product of the *Pterocarpus santalinus* (Linn.), a papilionaceous tree growing in tropical Asia. It is, or was, imported from the East Indies, Ceylon, the coasts of Coromandel and Malabar, Golconda, Madagascar, &c. It comes into commerce in the form of hard heavy billets of a dull red colour. In the state of powder it gives off a faint aromatic odour like that of orris root, specially noticeable when it is heated or boiled with water. It yields to alcohol about 19·6 p.c. of extract, mainly consisting of colouring matter which is sparingly soluble even in boiling water, though readily in alcohol.

The resinous colouring matter was first isolated from Sanderswood by Pelletier (*Ann. Chim.* 1832, [ii.] 51, 193), who termed it *sandel red*, and assigned to it the formula $\text{C}_{16}\text{H}_{16}\text{O}_3$. Meier (*Arch. Pharm.* 1848, 55, 285; 56, 41) named the colouring matter he obtained *santalac acid* or *santalin*, and though he did not analyse it, considered it to be a purer form of Pelletier's 'sandel red.' Meier extracted the wood with ether, evaporated the solution, and washed the residue with water. The impure product was dissolved in alcohol, the colouring matter precipitated by means of lead acetate, and the lead salt was collected and well washed with alcohol. In alcoholic suspension this lead compound was then decomposed by dilute sulphuric acid, and the clear liquid, after removal of the lead sulphate, was evaporated to crystallisation. Thus obtained, the santalin consisted of minute red crystals, m.p. 104° , insoluble in water but very soluble in alcohol. Sulphuric acid dissolved it with a dark red tint and caustic alkalis with a purple colour. Somewhat later Weyermann and Haffely (*Annalen*, 1850, 74, 226) suggested for santalin the formula $\text{C}_{15}\text{H}_{14}\text{O}_5$, though Franchimont and Sicherer again (*Ber.* 1879, 12, 14) considered the formula $\text{C}_{17}\text{H}_{16}\text{O}_6$ preferable. These latter authors who adopted a process very similar to that devised by Meier,

could not obtain santalin in a crystalline condition, though this melted at 104° – 105° . Fused with caustic potash the amorphous product gave *acetic acid*, *resorcinol*, and probably also *protocatechuic acid* and *catechol*, and when heated with hydrochloric acid at 180° methyl chloride was evolved. Nitric acid gave oxalic acid and a yellow bitter substance, probably *picric* or *styphnic acid*, and when oxidised with permanganate, a crystalline substance having a strong odour of *vanillin* together with oxalic and acetic acids was produced. Weidel (Zeitsch. für Chem. 1870, 6, 83) extracted the wood with boiling dilute alkali, neutralised the solution with hydrochloric acid and collected and dried the voluminous brick-red precipitate. By long-continued extraction with ether he obtained from this two crystalline substances, *santal* $2C_8H_6O_3 \cdot 3H_2O$, which is colourless, and a bright red compound, $C_{14}H_{12}O_4$.

Santal crystallised from alcohol in colourless rectangular plates, sparingly soluble in alcohol, soluble in caustic alkaline solutions, with a pale yellow colour. With alcoholic ferric chloride a red coloration was produced. When treated with bromine, a crystalline bromo-compound $C_8H_4Br_2O_3$ was obtained, and by fusion with alkali, *protocatechuic acid* was produced.

The compound $C_{14}H_{12}O_4$, which is very sparingly soluble in boiling alcohol, was obtained as a red crystalline powder possessing a green metallic lustre. It dissolved in caustic alkalis with a reddish-purple colour, and in sulphuric acid with an orange tint. Perkin (Chem. Soc. Trans. 1899, 75, 443) obtained from the commercial santalin of Merck of Darmstadt, by the employment of alcoholic potassium acetate, a potassium salt which on analysis agreed with the formula $C_{30}H_{27}O_5K$.

Cain and Simonsen (Chem. Soc. Trans. 1912, 101, 1061) give two methods for the preparation of santalin from the wood, and also for its subsequent purification. In one case an alcoholic, and in the second an ethereal extract was employed, and in both instances the colouring matter was isolated by means of its lead salt. The product from the former process was converted into potassium salt and the colouring matter obtained by its decomposition repeatedly crystallised from alcohol, whereas that obtained by the latter method was crystallised only from dilute alcohol. Santalin thus prepared consisted of a bright red micro-crystalline powder which softened at 223° and melted to a deep red oil at 226° . It possessed the formula $C_{14}H_{11}O_4OMe$, and gave with potassium acetate the salt $C_{30}H_{27}O_{10}K$.

When santalin is acetylated, *diacetylsantalin* $C_{15}H_{12}O_5(C_2H_3O)_2$, a reddish-brown micro-crystalline powder, is obtained, whereas by acetylation in presence of sodium acetate and zinc-dust a compound $C_{21}H_{20}O_8$, isolated as a pale brown powder, m.p. 242° – 243° , is produced, and this appears to contain three acetyl groups. Santalin methylated by means of methyl sulphate and aqueous alkali gives *santalin dimethyl ether* $C_{15}H_{12}O_3(OMe)_2$, a red, micro-crystalline powder, m.p. 165° – 167° , and a second compound $C_{16}H_{16}O_5$, m.p. 248° – 250° . The latter is obtained in much larger quantity when the operation is carried out in alcoholic solution.

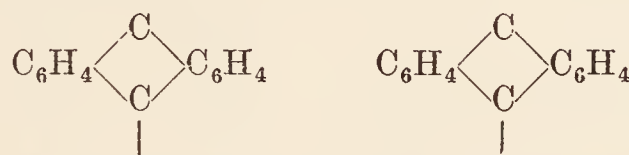
By oxidation with permanganate, santalin dimethyl ether gives *butyric*, *veratric*, and *anisic acids*.

Nitro-diacetyl-santalin $C_{19}H_{17}O_9N$, scarlet micro-crystalline powder, m.p. 180° – 181° ; *di-benzoyl-santalin* $C_{29}H_{22}O_7$, brown-red powder; *santalin oxime* $C_{15}H_{15}O_5N$, red powder; and *benzene-azo-santalin* $C_6H_5 \cdot N_2 \cdot C_{15}H_{13}O_5$, purple powder, have also been described.

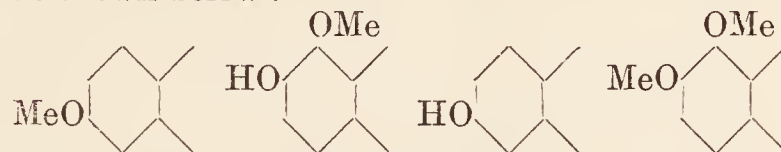
In a later paper (*ibid.* 1914, 105, 1335) Cain, Simonsen and Smith consider that the formula $C_{15}H_{14}O_5$ originally assigned by them to santalin should be doubled. Thus *santalin monomethyl ether*, the second product of the methylation of santalin referred to above, gives, similarly to the dimethyl ether when oxidised, *anisic* and *veratric acids*, and therefore cannot possess the simple formula $C_{14}H_{10}O_5(OMe)_2$.

Again, by oxidation in the same way, *nitrosantalin dimethyl ether* yields *anisic acid*, 4-nitro : 2 : 3-dimethoxybenzoic acid and two other acids at present unidentified.

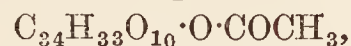
According to Grandmougin, santalin on distillation with zinc-dust yields *anthracene*, and though Cain, Simonsen and Smith were unable to confirm this result, they are inclined to the opinion that it is possibly a di-anthracene derivative, thus—



It is also suggested in their paper that the monomethyl ether yielding as it does *anisic* and *veratric acids*, has an unsymmetrical formula in which the two hydroxyls and four methoxy groups are distributed in the four benzene rings as shown below :—



By the reducing acetylation of santalin dimethyl ether the compound



m.p. 192° , is obtained, and by this reaction one ketonic group appears to have been reduced, and subsequently to have undergone acetylation. *Ethyl-carbonato-santalin* $C_{30}H_{26}O_{10}(CO_2Et)_2$, a red-brown powder, has also been obtained by these authors.

O'Neill and Perkin (Chem. Soc. Trans. 1918, 113, 125) isolated the colouring matter from an alcoholic solution by means of strong aqueous baryta, thus avoiding the very tedious filtrations involved by the lead acetate method. The crude product thus obtained is submitted to a fractional separation, for which purpose ethyl acetate and ether are mainly employed, and as a result these authors consider that at least two colouring matters, *santalin* and *deoxysantalin*, are present in this dyewood.

Santalin obtained by this method consists of a chocolate-coloured powder which when heated softens at 243° , decomposes at 250° – 260° , and at 270° is converted into a honeycombed carbonaceous mass. The formula $C_{24}H_{22}O_8$ is proposed for this substance rather than the $C_{30}H_{28}O_{10}$ adopted by Cain and Simonsen, whereas the potassium compound given by

potassium acetate is represented either as $C_{96}H_{87}O_{32}K$ or $C_{72}H_{65}O_{24}K$. *Acetylsantalin* $C_{24}H_{18}O_8(C_2H_3O)_4$, on heating commences to decompose at about 225° , and at 250° – 260° yields a carbonaceous mass.

Deoxysantalin, the more soluble colouring matter, to which the formula $C_{24}H_{24}O_7$ is tentatively assigned, consists of a bright red powder, the solution of which in ether exhibits a greenish fluorescence. Unlike santalin, the alcoholic solution gives no immediate precipitate with potassium acetate, and only by means of excess of the reagent, or on keeping, does a gelatinous deposit separate. Its colour reactions, employing alcoholic hydrobromic acid, alcoholic ferric chloride, and sodium hydroxide solution, are of a much yellower character than those given by santalin with these reagents. *Acetyl deoxysantalin* $C_{24}H_{20}O_7(C_2H_3O)_4$ forms an almost colourless powder very distinct in appearance from acetylsantalin. A molecular weight determination of acetylsantalin employing naphthalene as solvent made by these authors gave the extremely high figure 2558. This approximates to that given in a similar way by acetyl-iso-santalin (*l.c.* Camwood), but the inference to be drawn from these results is doubtful, in that the naphthalene solution may be of a colloidal character. According to O'Neill and Perkin, deoxysantalin is possibly the santalin described by Meyer, and may still contain some impurity which has hitherto prevented its isolation in a crystalline condition. The shades given by santalin and deoxysantalin on mordanted woollen fabrics are of a very similar character to those given by sanderswood itself and are referred to in the article on Camwood.

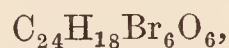
O'Neill and Perkin point out that the dyeing property of sanderswood seems to be due rather to deoxysantalin than to santalin, and although sanderswood is specially rich in colouring matter, it is astonishing how little of this comes into play during the dyeing process. Proof of this is obtained by dyeing wool with 60 p.c. of sanderswood and at the end of the operation employing the residual wood twice for dyeing fresh material. The first pattern possessed the usual colour, the second was pale pink, and the third was practically undyed, indicating that all the colouring matter soluble in water had then been removed. The woody matter, however, now yielded to alcohol 13.8 p.c. of extract compared with the 19.4 p.c. originally present, and this consisted of a dark-red resinous mass and contained much santalin. Even, therefore, if it be presumed that all the soluble matter removed from the wood in the dye-bath is colouring matter (and this is improbable), it is evident that the larger proportion present therein, owing to its insoluble nature, remains undissolved and takes no part in the operation. Attempts to isolate Weidel's compounds (*l.c.*) from sanderswood were unsuccessful.

In addition to colouring matter, sanderswood contains two neutral compounds, *Pterocarpin* and *Homo-ptero-carpin*, which were first isolated by Cazeneuve and Hugounenq (Compt. rend. 1874; 104, 1722). These authors extracted a dried mixture of the wood and slaked lime with ether, and the product which remained on evaporating the ether was crystallised, first

from alcohol and then fractionally so from carbon disulphide.

Ptero-carpin, the more sparingly soluble compound, and to which the formula $C_{20}H_{16}O_6$ was assigned, consisted of colourless plates, melting with previous softening at 152° . It is insoluble in alkalis and acids and possesses the specific rotatory power of $[\alpha_D] = -211$. By the action of bromine, in presence of carbon disulphide, it yielded *bromoptero-carpin* $C_{20}H_{15}BrO_6$, and this crystallised from a mixture of alcohol and benzene in fine needles. Smith (Philippine Journal of Science, 1910, 5, 451) has, however, shown that the correct formula of pterocarpin, also present in Narrawood, is $C_{14}H_{12}O_4$, and its m.p. 163° .

According to Cazeneuve and Hugounenq, *Homoptero-carpin*, which is somewhat readily soluble in carbon disulphide, melts at 82° – 86° , has the formula $C_{24}H_{24}O_6$, and in an approximately 5 p.c. solution in chloroform, its specific rotation is $[\alpha_D] = -199$. By bromination it yielded *bromohomoptero-carpin* $C_{24}H_{23}BrO_6$, amorphous, and *hexabromohomoptero-carpin*



crystallising in plates, whereas with nitrous acid an unstable *nitroso-* derivative, $C_{24}H_{23}(NO)O_6$, was obtained. Fuming nitric acid gave *trinitro-orcinol* and fusion with potassium hydroxide *phloroglucinol*. When heated with hydriodic acid, methylic iodide was evolved, and was evidence of the presence of methoxy groups.

Brooks (*l.c.*), who also isolated homoptero-carpin (m.p. 86°) from Narrawood, has assigned to it the formula $C_{17}H_{16}O_4$, and finds that when fused with alkali it gives *resorcinol*, and when distilled with zinc-dust *resorcinol dimethyl ether*. Ryan and Fitzgerald (Proc. Roy. Irish Acad. 30, 1913, 106), who obtained homoptero-carpin (m.p. 88°) from barwood, also adopted the formula $C_{17}H_{16}O_4$, but could only obtain from it a *dibromo-* derivative $C_{17}H_{14}Br_2O_4$, which crystallised in colourless needles, melting at 200° . Contrary to Cazeneuve's statement, it contains no methoxy group, but nevertheless a phenolic substance is obtained from it by the action of hydriodic acid. Again, the specific rotatory power previously assigned to it by the latter author is too low, and in an approximately 4 p.c. solution in chloroform is $[\alpha_D]_{20^\circ C} = -211^\circ$. Ryan and Fitzgerald consider it possible that homoptero-carpin is a derivative of chromane or cumarane. A. G. P.

SANDIVER. (Fr. *Suint de verre*.) The scum formed on the surface of the molten glass in the glass pots; known also as *glass gall* (*v.* GLASS).

SANDMEYER REACTION *v.* DIAZO COMPOUNDS.

SANDSTONE. (*Grès*, Fr.; *Sandstein*, Ger.) A granular siliceous rock, consisting of consolidated sand. If the cohesion is imperfect, the friable mass is sometimes known as *sand-rock*. The consolidation of the grains of quartz may be effected either by pressure, or by deposition of mineral matter forming an agglutinating medium between the grains. When the cement is siliceous, the resulting rock (*v.* QUARTZITE) has great hardness and durability, but is difficult to work. Where the grains are united by calcium carbonate, a *calcareous sandstone* is produced;

such a rock may be readily worked as a freestone, but by weathering it is apt to lose the calcareous cement, and, becoming more or less cavernous in texture, tends to suffer disintegration. In an *argillaceous sandstone* the cement is clayey, and the stone is not generally durable as a building material. In a *micaceous sandstone* scales of mica are present, and in many cases facilitate the splitting of the stone along the planes of bedding, as in the Yorkshire flagstone. A *felspathic sandstone* contains grains of felspar, either crystalline or more or less kaolinised, in addition to quartz; much of the Millstone Grit of England is of this character, having clearly resulted from the disintegration of granitic rocks. The term *arkose* is often applied to a sedimentary rock made up of the constituent minerals of granite, rearranged by deposition in water.

Ferruginous sandstones—especially those of the Old Red Sandstone, the Permian, and the Trias—present various tints of red and brown, due to the presence of ferric oxide, or its hydrate, acting as a cement, and forming a thin pellicle around each grain of quartz. Green sandstones, such as those of the Upper Greensand of Surrey, owe their colour to dark grains of glauconite (*q.v.*). The bluish and greyish tints of many sandstones are referred to the presence of ferrous carbonate, or of finely-divided iron-pyrites, or even to iron phosphate. Sandstones which are 'blue hearted' usually assume yellow or brown tints where exposed to oxidising influences. Grains or crystals of iron-pyrites in a sandstone are apt to produce rusty blotches when weathered. (On the colour of sandstones, *v. G. Maw*, Quart. Journ. Geol. Soc. 1868, 24, 351.)

If the component grains of quartz are sharp, the rock is termed a *grit*; many grits are valued as grindstones, while if very fine in texture they may sometimes be used as whetstones. A coarse grit may be employed as a millstone. Another variety of sandstone known as *ganister* (*q.v.*) is much used for refractory bricks and furnace linings. Sandstones used for building and paving purposes range in sp.gr. from 1.9 to 2.8, porosity 5–28 p.c., and crushing strain 130–1470 (average 400–700) tons per square foot.

The following are analyses¹ of sandstones from various British localities where the stone is quarried for building purposes: I, Dull-red, medium-grained micaceous 'Red Wilderness stone' from Mitcheldean quarries, Gloucestershire (Old Red Sandstone age). II, Brown, coarse-grained, slightly micaceous freestone from Prudham quarries, Northumberland (Carboniferous Limestone age). III, Dark blue-grey, very fine and compact 'Shamrock stone' from Doonagore quarries, Co. Clare (Millstone Grit age). IV, Yellow, medium-grained, slightly micaceous 'Hard York stone' from Crosland Hill quarries, Huddersfield, Yorkshire (Coal Measures). V, Light red, fine-grained, calcareous 'Red Mansfield stone' from Mansfield, Nottinghamshire (Permian). VI, Light yellow, fine-grained calcareous 'White

Mansfield stone' from Mansfield, Nottinghamshire (Permian).

	I.	II.	III.	IV.	V.	VI.
SiO ₂	88.70	86.40	84.90	93.30	49.4	51.4
Al ₂ O ₃	3.25	6.45	6.60	0.44	3.2	1.3
Fe ₂ O ₃	1.80	0.75	3.60	2.85		
FeO	0.30	—	—	—	—	—
MnO	0.10	—	0.65	—	—	—
CaO	2.90	0.60	0.90	1.46	14.8	14.8
MgO	0.11	0.27	1.26	1.32	7.8	8.6
K ₂ O	—	0.21	—	—	—	—
Na ₂ O	0.31	—	0.39	—	—	—
CO ₂	1.94	—	—	—	20.0	21.1
H ₂ O	0.59	5.25	1.70	0.33	4.8	2.1
Sp.gr.	100.00	99.93	100.00	99.70	100.0	99.3
Crushing strain, tons per sq. ft.	2.26	2.29	2.7	2.60	2.30	2.25
	695	455	1902	—	592	46

It has been shown by F. Clowes (Proc. Roy. Soc. 1889, 44, 363; 1899, 64, 374) that in certain Triassic sandstones, like the 'hemlock stone,' near Nottingham, the grains of sand are cemented by barium sulphate. Other cementing materials of rare and local occurrence are dolomite, gypsum, fluor-spar, bitumen, celestite, phosphorite, &c. Certain sandstones are impregnated with metallic compounds, rendering them useful as ores: thus, the Lower Keuper sandstones of Alderley Edge and of Mottram St. Andrew in Cheshire have yielded copper carbonates, both green and blue, with galena and cerussite, cobalt and manganese ores, mottramite, and vanadinite. The workable part of the metalliferous sandstone contained an average of 1.4 p.c. of copper; this was dissolved out by dilute hydrochloric acid, and precipitated by scrap iron (Greenwell, Proc. S. Wales Inst. Eng. 1866, 4, 44; Hull, Geol. Mag. 1864, 1, 65). Native copper is disseminated in a granular form through certain sandstones at Lake Superior. The Bunter sandstone, near Commern, in the Eifel, contains valuable deposits of lead-ore, usually sulphide, although sometimes carbonate, occurring in nodules, whence the rock is termed *Knottensandstein*. Many iron ores of the secondary rocks, like those of Northamptonshire and Lincolnshire, are so siliceous as to pass into highly ferruginous sandstones.

References.—J. A. Howe, The Geology of Building Stones, London, 1910; J. Watson, British and Foreign Building Stones, Cambridge, 1911; for American sandstones, *v. G. P. Merrill*, Smithsonian Rep. for 1886, part 2, 443; Stones for Building and Decoration, 3rd ed., New York, 1903.

L. J. S.

SANGA-SANGA OIL is obtained from the nuts of *Ricinodendron africanum* (Nat. ord. Euphorbiaceæ) found in the Lower Congo, and also in the French Congo and Gabon, where it is known as 'essang,' 'engnessang,' or 'issanguila.' In other parts of Equatorial West Africa it is known as 'usa sana.' The kernel yields 55 p.c. of oil, limpid, pale yellow, and of a sweet flavour, with no special odour. Its refractive index is higher than that of any other known vegetable oil save abrasin oil. It is a drying oil, solidifying more rapidly than linseed oil. For analytical characters, see Analyst, 1918, 295.

SANGUINARINE C₂₀H₁₅O₄N occurs in *Sanguinaria canadensis* (Linn.) and other papaveraceous plants (Fischer, Arch. Pharm. 1901, 239, 409, 421; and Schmidt, *ibid.* 395).

¹ Quoted from Watson (*l.c.*). For other analyses, see J. A. Phillips (Quart. Journ. Geol. Soc. 1881, 37, 21); W. Mackie (Trans. Geol. Soc., Edinburgh, 1901, 8, 33); P. Holland and E. Dickson (Proc. Liverpool Geol. Soc., 1896, 7, 443).

It is a colourless, optically inactive, crystalline monacidic base, m.p. 212° , forming red crystalline salts (König, Chem. Soc. Abstr. 1891, i, 843). For the separation from β - and γ -chelidonine, chelerythrine and protopine which accompany it, see Kózniewski (Bull. Acad. Sci. Cracow, 1910, 235; Chem. Soc. Abstr. 1910, i, 874). Exerts a narcotic action, but causes tetanus and excitement. G. B.

SANIDINE *v.* FELSPAR.

SANOFORM *v.* SALICYLIC ACID and SYNTHETIC DRUGS.

SANTALENE $C_{15}H_{24}$ is contained in East Indian sandalwood oil (*Santalum album* [Linn.]). It is a mixture of the isomeric α - and β -santalenes.

α -Santalene is a tricyclic sesquiterpene; it forms a colourless oily liquid with a faint odour, b.p. 118° – $120^{\circ}/9$ mm., sp.gr. 0.8984 at 20° , $\alpha_D - 15^{\circ}$ (100 mm. tube). When oxidised with ozone, it yields *tricyclic eksantalal* $C_{11}H_{16}O$, and when treated with glacial acetic acid in a sealed tube at 180° – 190° it forms an α -acetate, b.p. 164° – $165^{\circ}/14$ mm.

α -Santalene also yields an α -nitrosochloride $C_{15}H_{24}NOCl$, m.p. 122° , and an α -santalenenitrol-piperidine $C_{15}H_{23} \begin{smallmatrix} NOH \\ \diagup \\ C_5H_{10}N \end{smallmatrix}$, m.p. 108° – 109° .

β -Santalene is a bicyclic sesquiterpene and closely resembles the α - compound, b.p. 125° – $127^{\circ}/9$ mm., D_{20} 0.892, $\alpha_D - 35^{\circ}$, when oxidised with ozone it yields *bicyclic eksantalal*, and treated with glacial acetic as above it gives a β -acetate $C_{15}H_{25}O \cdot COMe$, b.p. 164° – $168^{\circ}/14$ mm. β -Santalene yields two *nitrosochlorides*, m.p. 152° and 106° respectively, the former being less soluble in alcohol than the latter. Each of these nitrosochlorides yields a *nitrolpiperidine*, m.p. 101° and 104° – 105° respectively.

When β -santalene is treated with glacial acetic acid and sulphuric acid, it yields a *sesquiterpene alcohol* $C_{15}H_{25}OH$, which has a strong odour of cedar and has b.p. 160° – $165^{\circ}/6$ mm.

Santalene dihydrochloride $C_{15}H_{24} \cdot 2HCl$, obtained by the addition of hydrogen chloride to santalene in methyl alcohol has b.p. 140° – $142^{\circ}/0.55$ mm., and sp.gr. 1.076 at 20° . When boiled with alcoholic potash, it yields β -santalene. When treated with sodium and boiling alcohol the dihydrochloride yields a mixture of hydrocarbons which when treated with ozone gives pure *tetrahydrosantalene* $C_{15}H_{28}$, b.p. 116° – $118^{\circ}/9$ mm., sp.gr. 0.864 at 20° , $\alpha_D + 7^{\circ} 30'$ (100 mm. tube). This hydrocarbon is dicyclic and is analogous to dihydroeksantalol and to dihydroeksantallic acid (Semmler, Ber. 1910, 43, 445).

Literature on the santalenes: Soden and Müller, Pharm. Zeit. 1899, 44, 258; Chem. Zentr. 1899, i, 1082; Arch. Pharm. 1900, 238, 149, 353; Guerbet, Compt. rend. 1900, 130, 417, 1324; Semmler, Ber. 1907, 40, 3321.

SANTALIC ACID. *Santalin* *v.* SANDERSWOOD.

SANTALOL $C_{15}H_{23}OH$, often known in commerce as *Gonorol*, is the chief constituent of East Indian sandalwood oil from which it is obtained by distilling the latter in steam, converting the oil in the distillate into the hydrogen phthalate and then hydrolysing this ester: or sandalwood oil is saponified and the product submitted to fractional distillation *in vacuo*,

or with superheated steam. By simple fractional distillation, the alcohol cannot be obtained pure (D. R. PP. 110485, 116815; Frdl. 1897–1900, 917; see also Soden, Arch. Pharm. 1900, 238, 353; Müller, *ibid.* 366).

Thus obtained it has b.p. 161° – $168^{\circ}/10$ mm., sp.gr. 0.973 at 20° , $\alpha_D - 21^{\circ}$ (100 mm. tube). By repeated fractionation it can be separated into its two chief constituents, the isomeric α - and β -santalols.

α -Santalol is the chief constituent of commercial santalol. It is a tricyclic sesquiterpene alcohol, b.p. 301° – 302° , 159° – $160^{\circ}/10$ mm., sp.gr. 0.978 at 20° , $[\alpha]_D + 1^{\circ}$ to $+2^{\circ}$.

β -Santalol is a bicyclic sesquiterpene alcohol, b.p. 309° – 310° , 167° – $168^{\circ}/10$ mm., sp.gr. 0.9715 at 20° , $\alpha_D - 42^{\circ}$ (Guerbet, Compt. rend. 1900, 130, 1324; Semmler, Ber. 1910, 43, 1894).

If the mixture of α - and β -santalols, as it occurs in commerce, is carefully fractionated a partial separation of the two isomerides can be effected. If each of these is converted into the hydrogen phthalate, and this again into the strychnine salt, recrystallisation of this salt can be continued until m.p. and rotatory power are constant, when saponification yields the pure isomeride. The *strychnine phthalate* of β -santalol

$C_6H_4(CO_2 \cdot C_{15}H_{23})(CO_2H, C_{21}H_{22}O_2N_2)$ has $[\alpha]_D - 30.43^{\circ}$, m.p. 134° – 135° , and the β -santalol obtained from it has b.p. 168° – $169^{\circ}/10$ mm., D^{15} 0.9729, n_D^{19} 1.5092, $[\alpha]_D - 42.00^{\circ}$.

The *strychnine phthalate* of α -santalol has m.p. 155° , $[\alpha]_D - 1.40^{\circ}$. The α -santalol prepared from it has b.p. $159^{\circ}/10$ mm., D^{15} 0.979, n_D^{19} 1.499, $[\alpha]_D + 1.10^{\circ}$ (Paolini and Divizia, Atti R. Accad. Lincei, 1914, [v.] 23, ii, 226).

When crude santalol is oxidised with potassium permanganate santalal and eksantallic acid are formed as chief products.

Santalal, santalaldehyde $C_{15}H_{22}O$, has b.p. 152° – $155^{\circ}/10$ mm., sp.gr. 0.995 at 20° , $[\alpha]_D + 13^{\circ}$ to $+14^{\circ}$, and contains a very small quantity of *l*-santalal. *Santalal semicarbazone* has m.p. 230° , and the *oxime* m.p. 104° – 105° , b.p. 182° – 185° . When the latter is boiled with acetic anhydride it yields the *nitrile* $C_{15}H_{21}N$, b.p. 162° – $166^{\circ}/9$ mm., sp.gr. 0.990 at 20° , $[\alpha]_D + 14^{\circ}$, which when saponified gives *santolic acid* $C_{15}H_{22}O_2$, b.p. 192° – $195^{\circ}/9$ mm.

When crude santalol is oxidised with ozone and the product distilled with steam, *eksantol oxide*, m.p. 157° , and chiefly *eksantalal* $C_{12}H_{18}O$, b.p. 109° – $110^{\circ}/10$ mm., are formed. By a similar process to that described above, it can be converted into *eksantallic acid* $C_{12}H_{18}O_2$, m.p. 68° , b.p. 161° – $163^{\circ}/10$ mm. This acid is also formed as above and as a by-product in the oxidation of santalol with ozone. By the reduction of its methyl ester, *dihydroeksantallic acid* is formed, b.p. 164° – $166^{\circ}/10$ mm., m.p. 58° , the methyl ester of which when reduced yields *dihydroeksantalol* $C_{12}H_{22}O$, b.p. 130° – 132° .

When eksantalal is treated with acetic anhydride it forms an *enol acetate*, which on oxidation with potassium permanganate yields *noreksantallic acid* $C_{11}H_{16}O_2$, m.p. 93° , b.p. 143° – $145^{\circ}/10$ mm.; the methyl ester of this acid gives on reduction *noreksantalol* $C_{11}H_{18}O$, b.p. 114° – $117^{\circ}/10$ mm., which when oxidised with

chromic acid gives *noreksantalol*, m.p. 92°–94°. This yields an enol acetate, b.p. 110°–113°/10 mm., which, when oxidised with permanganate in aqueous acetone, gives *teresantallic acid* $C_{10}H_{14}O_2$, m.p. 156°, and from this by reduction *teresantalol* $C_{10}H_{16}O$, m.p. 114°, is obtained. All these derivatives are tricyclic or α -compounds, but may in many cases be converted into the corresponding bicyclic or β -compound, by treatment with hydrogen chloride and subsequent saponification (Semmler and Zaar, Ber. 1910, 43, 1890; Semmler, *ibid.* 1722, 1893; see also Semmler, *ibid.* 1909, 42, 584; *ibid.* 1908, 41, 1488; *ibid.* 1907, 40, 1120; Semmler and Bartelt, *ibid.* 1907, 40, 3101, 4465; *ibid.* 1908, 41, 385, 866; Chapman and Burgess, Chem. Soc. Trans. 1901, 134; Müller, *l.c.*).

In addition such hydrocarbons as *noreksantalane* $C_{10}H_{16}$, &c., have been obtained from santalol (Semmler and Bode, Ber. 1907, 40, 1124).

When heated in a sealed tube with alcoholic potash, α -santalol yields *eksantalol* $C_{12}H_{20}O$.

Santalyl halides are obtained by treating santalol or sandalwood oil with phosphorus halides or with phosgene in presence of bases, or by heating santalol halogen carbonate (D. R. P. 203849; Frdl. 1907–10, 918; Semmler and Bode, *l.c.*).

Santalyl chloride is an oil, b.p. 162°–167°/15 mm. pressure. The halides are used in perfumery and in medicine.

Santalyl carbonate (Blenal) is prepared by heating together equal parts of guaiacol carbonate and santalol *in vacuô* at 170°–180° until no more guaiacol distils over or by heating santalol (200 grms.) with phenyl carbonate (100 grms.) and caustic soda (2 grms.) under diminished pressure at 140°–175°. The carbonate is then purified by washing and redissolving in dilute alcohol (Eng. Pat. 20586, 1906).

Santalyl ethyl carbonate is prepared by condensing santal oil with ethyl chlorocarbonate in pyridine. It boils at 180°–185°/25 mm., and has sp.gr. 1.010 at 15°.

Santalolsalacetolcarbonate, formed by the action of a chloroform solution of santalol on salacetol chlorocarbonate, in the presence of pyridine, is a pale yellow syrupy liquid, with a faint aromatic odour soluble in chloroform, benzene, and ether, almost insoluble in water (D. R. P. 206055; Frdl. 1907–10, 944).

The santalyl esters of the fatty acids $C_nH_{2n}O_2$ and $C_nN_{2n-2}O_2$ (where n = not less than 5) are prepared in the ordinary way and are said to be free from the objectionable taste of santalol, and of its esters with the lower fatty acids (D. R. P. 182627; Frdl. 1905–7, 942). For some of the lower esters, see D. R. PP. 201369, 191547 (*cf.* Riedel, D. R. P. 275794).

Mixed santalyl esters of dibasic acids are obtained by heating santalol with the anhydride of the required acid at 100°–120°, and then alkylating the resulting santalyl acid (D. R. P. 208637; Frdl. 1907–10, 922).

Methyl santalylsuccinate is an oil of sp.gr. 1.058 at 25°.

Methyl santalylphthalate has sp.gr. 1.085, and *methyl santalylcamphorate* (Camphoral) has sp.gr. 1.04 (*see also* D. R. P. 193960).

The santalyl esters of monobasic aromatic acids are prepared by the action of the acid

chlorides, anhydrides or esters on santalol. They are non-irritant and do not possess the disagreeable taste of santalol or of its acetyl and phthalic acid derivative (D. R. PP. 173240, 18725; Frdl. 1905–7, 939, 941).

The *santalyl ester of allophanic acid* (Allosan) $C_{15}H_{23} \cdot CO_2 \cdot NH \cdot CO \cdot NH_2$ is prepared by the prolonged action of cyanic acid on santalol in benzene solution or by the action of urea chloride, phenol carbamate or phenol allophanate on santalol (D. R. P. 204922; Frdl. 1907–10, 921). It melts at 162° and is tasteless and odourless, is soluble in most organic solvents, but not in water.

Santalyl ethers are obtained by treating santalyl halides with metal alcoholates or by treating santalol or sandalwood oil with alkylating agents (D. R. P. 202352).

Santalyl methyl ether (Thyreol), b.p. 149°–156°/16 mm., and *santalyl ethyl ether*, b.p. 169°–174°/22 mm., are colourless liquids.

Santalyl phenyl ether, b.p. 232°/20 mm., is a viscid oil, and the *menthyl ether*, b.p. 201°–210°/5 mm., is a colourless syrup.

Santalol combines with formaldehyde in presence of dilute mineral acids at 95°–100°, forming the compound $C_{16}H_{18}O_2$, a yellow balsam-like oil of antiseptic properties, sp.gr. 0.882, $[\alpha]_D$ 10.9° at 20° in chloroform. When distilled with warm water it decomposes into its constituents (D. R. P. 148944; Frdl. 1902–4, 69).

The *dialkylaminoacetyl santalols*, obtained by the action of halogen acetyl santalol on secondary amines, are said to be valuable in medicine owing to the fact that they form solid, odourless and readily assimilated salts (D. R. P. 226229; J. Soc. Chem. Ind. 1910, 1474).

SANTENE C_9H_{14} is a terpene contained in sandalwood oil (*Santalum album*, Linn.) (Müller, Arch. Pharm. 1900, 238, 366), in various pine needle oils, *Picea excelsa* (Link), and other oils (Aschan, Ber. 1907, 40, 4918). Santene may also be obtained by treating *teresantallic acid* with dilute sulphuric acid (Semmler, *ibid.* 4591), or by chlorinating π -norborneol and then splitting off hydrochloric acid (Semmler and Bartelt, *ibid.* 4466; *ibid.* 1908, 41, 125). It may also be prepared by the action of alcoholic potassium hydroxide or of aniline upon camphenyl chloride (Kompa and Hintikka, Bull. Soc. chim. 1917, [iv.] 21, 13). Santene is optically inactive, has b.p. 140°–141° or 31°–33°/9 mm., sp.gr. 0.863 at 20°, n_D 1.46658.

When oxidised in benzene solution with ozone or potassium permanganate, it yields *santene diketone* $C_8H_{14}O_2$, b.p. 124°–127°/9 mm., sp.gr. 1.024 at 20°, n_D 1.46658, its *dioxime* has m.p. 129° and the disemicarbazone has m.p. 216°. The diketone is oxidised by alkaline bromine solution to a *keto acid* $C_8H_{12}O_3$, b.p. 173°–175°/10 mm., yielding a semicarbazone, m.p. 182°. A series of other octene derivatives have been obtained from the diketone (Semmler and Bartelt, Ber. 1907, 40, 4595; *ibid.* 1908, 41, 869).

When treated with formic acid, santene yields π -norborneol formate, b.p. 82°–84°/9 mm., which, except for its being optically inactive, is identical with the product obtained by the interaction of *teresantallic acid* and formic acid (*ibid.* 125, 385).

Santenol acetate $C_9H_{15}O \cdot C_2H_3O$ is obtained by treating santene with glacial acetic and dilute sulphuric acids. It has b.p. 215° – 219° ; 88° – $89^\circ/8$ mm., sp.gr. 0.9871 at 20° , n_D 1.45929 at 19° , and when saponified forms *santenol* $C_9H_{16}O$, b.p. 195° – 198° , probably identical with π -norborneol. After distillation, santenol forms a solid which when recrystallised forms clear tablets or prisms, m.p. 97° – 98° . Its *phenyl-urethane* derivative has m.p. 61° – 62° ; when oxidised with chromic acid, santenol yields a *ketone*, m.p. 58° – 59° , the *semicarbazone* of which has m.p. 225° – 226° (Aschan, l.c.).

Santene glycol $C_9H_{14}(OH)_2$ is formed by dissolving santene in acetone, adding a little water and some powdered potassium permanganate, the whole is then distilled in steam and the distillate extracted with ether. It has m.p. 193° , b.p. $135^\circ/10$ mm., and when distilled with sulphuric acid yields a *ketone* $C_9H_{14}O$, b.p. 76° – $80^\circ/10$ mm. (Semmler and Bartelt, l.c. 868).

Santene hydrochloride $C_9H_{15}Cl$, m.p. 80° – 81° , is formed by passing hydrochloric acid gas into a cold ethereal solution of santene (Müller, l.c.; Aschan, l.c.).

Santene tribromide $C_9H_{13}Br_3$, m.p. 62° – 63° , is obtained by treating a chloroform solution of santene with bromine (Soden and Müller, Chem. and Druggist, 1900, 57, 282).

Santene nitrosochloride $C_9H_{14}NOCl$, m.p. 109° – 110° , is of a blue colour and passes into a white modification after a few hours. On heating to 80° – 90° the latter again becomes coloured and has then m.p. 110° – 111° (Müller, l.c.; Aschan, l.c.).

Santene nitrosite, m.p. 124° – 125° , has also been prepared (Müller, l.c.; Aschan, l.c.).

SANTHEOSE. Trade name for theobromine.

SANTONICA. Wormseed (*Semen-contra*, Fr.; *Wurmsamen*, Ger.). *Flores cinæ.* The so-called wormseed consists of the minute unexpanded flower-heads of *Artemisia maritima*, variety *Stechmanniana* (Besser) (v. Benth. a. Trim. 157). The species is widely distributed throughout Europe and Asia; but the variety which yields the more esteemed Levant wormseed of commerce is for the most part confined to southern Russia and Turkestan, especially the district of the lower Volga. Thence the drug enters European markets by way of Nijni Novgorod. The santonica shrub emits a marked camphoraceous odour, which is distinctly perceived in the drug itself when rubbed. The taste is bitter and aromatic (cf. Flückiger, Pharm. J. [iii.] 17, 449).

For the occurrence of santonin in *Artemisia brevifolia* (Wallich), found from Kashmir to Kurneon and in Western Tibet, see Greenish and Pearson, Pharm. J. 1921, 2.

An examination of samples of leaves, flower buds, etc., of *Artemisia brevifolia* showed that in collections made from July 8th to August 7th, 1922, at Garez, Kashmir, the proportion of santonin increased with the growth of the plant. The proportion of santonin in material received earlier in the year was 0.83 p.c., or 0.92 p.c. on the dry material, but the figures for the later samples were as follows: the first figure in each case representing the percentage of santonin on the wet material, and the second the figure on the dry material: (1) leaves and flower buds

(July 8th), 0.82 and 0.92; (2) leaves and flower buds (July 16th), 1.21 and 1.31; (3) flower buds (July 26th), 0.97 and 1.07; (4) flower buds (August 7th), 1.64 and 1.79 p.c. Sample (4) was found, on separation, to contain (a) in the flower buds and leaves (83 p.c. of sample) 1.95 p.c., and (b) in the stalks 1.19 p.c. of santonin. These figures show that *Artemisia brevifolia* compares favourably with *Artemisia maritima*, the usual source of santonin (Bull. Imp. Inst. 1923, 21, 316; Analyst, 1924, 49, 39; J. Soc. Chem. Ind. 1924, 43, 15). For the occurrence of santonin in *Artemisia gallica*, see Maplethorpe, Pharm. J. 1924, 113, 106.

Of 56 species of *Artemisia*, indigenous to America, pronounced tests for santonin were obtained from *A. mexicana*, Willd., from *A. neo-mexicana*, Wooton, and from *A. Wrightii*, all of which grow in the region of New Mexico and Mexico. The results indicate a distinct possibility of utilising American plants, growing as weeds in barren fields, as a source of santonin (A. Viehoveer and R. G. Capen, J. Amer. Chem. Soc. 1923, 45, 1941–1944; J. Soc. Chem. Ind. 1923, 42, 947, A).

Santonica is used in medicine almost exclusively for its powerful anthelmintic property in the case of the round lumbricoid worm *Ascaris lumbricoides*; but for this purpose its chief active constituent, santonin, has quite superseded the drug itself, and is now alone included in the British and United States Pharmacopœias. When santonin or santonica has been administered the urine assumes a saffron-yellow colour, changed to violet by alkalis, and in many cases the field of vision is suffused with a yellow hue. König finds that the visual power of recognising the ulterior portion of the blue and the entire extent of the violet of the solar spectrum is entirely abolished for the time being, whilst the point of neutrality is situated at the wave length of 573, this being the exact complementary point of the suppressed violet. König infers that the visual phenomena, occasioned by the ingestion of sodium santoninate, do not constitute actual violet blindness, the retina or optic nerve being affected, but that the rays of violet light are, during the santoninic toxic condition, simply absorbed by certain of the media of the eye, which have been abnormally, and, of course, only temporarily, affected by the drug (J. Soc. Chem. Ind. 1889, 566).

Santonin $C_{15}H_{18}O_3$ was discovered in santonica by Kahler in 1830 (Brandes Arch. 34, 318; 35, 216), and independently obtained immediately afterwards by Alms (Brandes Arch. 34, 319; 39, 190). It was further studied by Trommsdorff (Annalen, 11, 190), and by Heldt (*ibid.* 63, 10), and by many others (see below). To obtain it the volatile oil is extracted by light petroleum, and 200 grms. of the residue is then boiled with 70 grms. of slaked lime, 400 c.c. of water, and 400 c.c. of spirit; the treatment is twice repeated. This dissolves the santonin as calcium santoninate. After filtration and evaporation to 500 c.c. hydrochloric or acetic acid is added carefully to precipitate a brown resin. On separating this and excess of hydrochloric acid added, santonin is reformed and soon crystallises out. It is recrystallised from 10 parts of alcohol with charcoal. The crystallisation has

to be effected in a dark place, otherwise the product is converted by the actinic rays into a yellow compound, which, at least in those cases where the alcohol is not free from water, is the ethyl ether of a new dibasic acid *photosantoninic acid* $C_{15}H_{22}O_5$ (Sestini, Gazz. chim. ital. 6, 357); for absorption spectra *v.* Piutti (Atti R. Accad. Lincei, 1913, [v.] 22, ii. 192); Mayer (*ibid.* 1914, [v.] 23, i. 442). The yield of santonin varies from 1 to 3 p.c. For the preparation of santonin, see also Busch (J. pr. Chem. [ii.] 35, 322) and Cech (Dingl. poly. J. 253, 474), and for detection of santonin, Manseau (Chem. Zentr. 1891, ii. 733).

For estimation of santonin in santonica, see Katz (Arch. Pharm. 1899, 237, 245, and Allen's Commercial Organic Analysis, 1913, vii. 155); Kariyone and Kimura (Pharm. Soc. Japan, 1920, 927; J. Chem. Soc. 1921, 120, ii. 223); Analysis of Santonin Tablets, François (J. Pharm. chim. 1922, 26, 339; Analyst, 1923, 30).

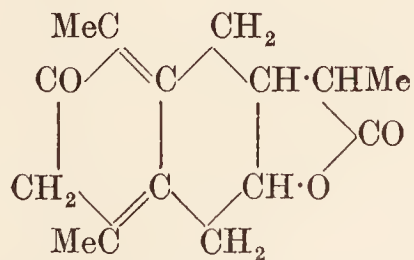
Santonin crystallises from water in flattened hexagonal prisms and from ether in rhombic plates. It melts at 171° – 172° , and when heated to a higher temperature in small quantities it may be sublimed. 1 gram dissolves in 43 c.c. of alcohol, 1.7 c.c. of chloroform, and 110 c.c. of ether at 25° ; also in 6.5 c.c. of boiling alcohol (U.S. P.). It is soluble in 250 parts of boiling and 5000 parts of cold water (Trommsdorff); $[\alpha]_D$ in alcohol -173.8° , in chloroform -171.4° . If a small fragment of santonin be dissolved in cold sulphuric acid and a drop of ferric chloride solution be added, there is developed a beautiful crimson colour which passes over to purple and violet. A crimson colour is also obtained when santonin is treated with alcoholic potash (Heldt).

For the estimation of santonin in wormseed, five grms. of the wormseed are heated for 15 minutes on a steam-bath with 30 c.c. of water, after which 10 c.c. of dilute hydrochloric acid are added, and the heating continued for another 15 minutes. The mixture is then cooled and vigorously shaken for 5 minutes with 60 c.c. of chloroform, 5 grms. of tragacanth added, and the shaking repeated until the chloroform separates. The chloroform extract is filtered through cotton wool, 40 c.c. of the filtrate are distilled, and the residue is boiled for 10 minutes with 50 c.c. of 15 p.c. alcohol beneath a reflux condenser. The solution is filtered, the residue washed twice with 10 c.c. of the boiling dilute alcohol, and the filtrate and washings left for 24 hours in a weighed flask in a cool place and then weighed. The liquid is next filtered through a weighed filter, the crystalline deposit transferred to the filter by means of a jet of 3.5 c.c. of the alcohol, and washed twice with 10 c.c. of the same solvent, and the flask and filter dried at 100° – 105° C. An addition of 6 mgrms. is made to the weight of santonin for each 10 grms. of the liquid in the flask prior to the filtration. Ten samples of wormseed thus examined yielded from 1.55 to 3.36 p.c. of santonin (L. M. van den Berg, Pharm. Weekblad. 1923, 60, 858–870).

According to O. P. A. Schaap (Pharm. Weekblad, 1924, 61, 277) 5 grms. of the drug are dried in a desiccator and mixed with 1.5 grms. of slaked lime and sufficient water to form a paste. After standing 24 hours the mass is treated with 100 c.c. of water, and boiled for 30 minutes, after which a solution of 5.5 grms. of zinc sul-

phate in a little water is added, and the boiling continued for 10 minutes. The liquid is filtered, the filter and residue boiled for 15 minutes with 100 c.c. of water, and this new extract filtered. The united filtrates containing the santonin, probably in the form of zinc santoninate, are treated with 3 c.c. of 30 p.c. nitric acid and evaporated to dryness, and the residue treated with 25 c.c. of water and again evaporated. Ten c.c. of water and 2 grms. of calcium carbonate and a little sand are then added, and the mixture cooled, transferred to a separator, and shaken for 2 minutes with 50 c.c. of chloroform. The extract is filtered and 40 c.c. of the filtrate (=4 grms. of the sample) are evaporated, the residue dissolved in 5 c.c. of methyl alcohol, and the solution diluted with 35 c.c. of water at about 60° and left for 24 hours. The crystals of santonin are then collected on a weighed filter, washed with five successive quantities of 2 c.c. of water, and dried at 100° . By this method practically the whole of the resin acids in the drug is eliminated (Analyst, 1924, 49, 345).

The constitution of santonin has been chiefly investigated by Cannizzaro and various other Italian chemists and by E. Wedekind. For a résumé, see Die Santonin-gruppe, by the latter author, in Ahrens' Sammlung chemischer und chemisch-technischer Vorträge, 1903, and his paper in Arch. Pharm. 1906, 244, 623. L. Francesconi, in Santonina e suoi Derivati, Rome, 1904, gives a complete list of derivatives up to that date. Subsequent papers are Klein, Ber. 1907, 40, 939; Wedekind, *ibid.* 1908, 41, 359; 1914, 47, 2483; 1915, 48, 891; Wedekind and Beniers, Annalen, 1913, 397, 246; Francesconi and Cusmano, Atti R. Accad. Lincei, 1907, [v.] 17, i. 64, 207; Gazz. chim. ital. 1908, 38, ii. 101; Bargellini and Gialdino, Atti R. Accad. Lincei, 1907, [v.] 17, i. 248; Levi-Malvano and Mannino, *ibid.* 1908, [v.] 17, ii. 484; 18, ii. 144; Cusmano, *ibid.* 1912, [v.] 21, ii. 796; 1913, [v.] 22, i. 711; Annalen, 1913, 400, 332; Bargellini, Daconto and Mannino, Gazz. chim. ital. 1908, 38, ii. 41; Bargellini and Mannino, *ibid.* 1909, 39, ii. 101; Bargellini and Silvestri, *ibid.* 1909, 39, ii. 346; Angeli and Marino, Mem. R. Accad. Lincei, 1908, [v.] 6, 385; Angeli, Ber. 1913, 46, 2233; Asahina, *ibid.* 1913, 46, 1775; Wienhaus and von Öttingen, Annalen, 1913, 397, 219; Wienhaus, Ber. 1913, 46, 2836. Of the several constitutional formulæ which have been proposed for santonin (see *e.g.* Asahina, above) the most generally accepted is the subjoined, of Cannizzaro:



It is the lactone of santoninic acid, of which the calcium salt is formed in the process of extraction of the drug. The two double bonds are reduced by hydrogen and platinum black (Asahina), and the resulting tetrahydro derivative has been most studied of late. Angeli objects to the above formula, because he and Marino have obtained by oxidation a heptane tetra-carboxylic acid $C_6H_{12}(CO_2H)(CO_2H) \cdot C(CO_2H)_2$, and he

thus postulates the grouping $\begin{array}{c} \cdot\text{C} \quad \quad \cdot\text{C} \\ \quad \diagdown \quad \diagup \\ \quad \text{C} \\ \quad \diagup \quad \diagdown \\ \cdot\text{C} \quad \quad \cdot\text{C} \end{array}$, and a

bridge (as in camphor) which is broken in the transformation of santonin to derivatives of dimethylnaphthalene. For the physiological action of santonin derivatives, many of which have been used in medicine, see Coppolo (Chem. Soc. Abstr. 54, 310; Wedekind, Zeitsch. physiol. Chem. 43, 240).

Santonica contains, besides santonin and the substances found in all plants, certain volatile constituents. When distilled with steam 1 to 2 p.c. of a *volatile oil* passes over, which contains α -pinene, terpinene, terpineol, and terpinenol, and a sesquiterpene (b.p. 250° approx.) (Schimmel, Semi-Annual Rep. 1908; cf. Schindelmeiser, Apoth. Zeit. 22, 876). The last mother-liquors in the technical treatment of the seed of *Artemisia maritima* contain *artemisin* $\text{C}_{15}\text{H}_{13}\text{O}_4$. It is freed from santonin by recrystallisation from chloroform, being deposited in combination with 1 molecule of that solvent. Artemisin melts at 200° , gradually turns yellow in the air, and is more readily soluble in water or dilute alcohol than santonin, of which it is possibly a hydroxyl derivative (Merck, Chem. Zentr. 1895, i. 436). Hydroxy santonins also appear in the urine when santonin has been administered. G. B.

SANTONIN, SANTONINIC ACID v. SANTONICA.

SANTYL. Trade name for santalyl salicylate.

SAPAN- or **SAPPANWOOD** v. BRAZILWOOD.

SAPONARIA OFFICINALIS (Linn.). The epidermal cells of the leaves of certain flowering plants contain, dissolved in their cell sap, a substance which is coloured blue by iodine. The colour disappears on warming and returns on cooling, as is the case with starch. On this account the compound was regarded as an amorphous variety of starch by Sanio, its discoverer (Botanische Zeitung. 1857, 15, 420). Schenck (*ibid.* 1857, 15, 497, 455) doubted whether this substance was identical with starch, and the correctness of this view was confirmed by Nägeli (Beiträge zur wissensch. Botanik. 1860, 2, 187). For the chemical examination of this substance the dried shoots of the *Saponaria officinalis* were selected by Barger (Chem. Soc. Trans. 1906, 89, 1210) as the raw material, because this plant is relatively rich in the compound, and is grown on the Continent for pharmaceutical purposes, so that large quantities are easily obtainable.

Saponarin $\text{C}_{21}\text{H}_{24}\text{O}_{12} \cdot 2\text{H}_2\text{O}$. The material was extracted with from 10 to 20 times its weight of water for half an hour, and the operation repeated several times. The extracts, strained through linen and concentrated to a quarter their volume, were acidified with acetic acid and left to stand for several weeks. The grey deposit which had then separated was dissolved in hot 1 p.c. sodium carbonate solution (1 litre per kilo. of dry leaves), and after addition of acetic acid was treated with lead acetate, in order to precipitate gums and other impurities. On standing for several weeks the clear liquid deposited crude saponarin, which, however still contained 30 p.c. of impurity.

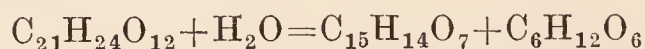
The crude saponarin was dissolved in boiling

pyridine, the dark brown solution was filtered and evaporated in a vacuum on the water bath. The residual syrup dissolved in hot water was diluted and on standing deposited the substance in microscopic needles.

Saponarin dried in air is a white powder, but after being dried in a vacuum becomes pale yellow, and is soluble in dilute alkaline solutions with an intense yellow colour. When heated slowly it melts and decomposes at 231° – 232° , but if the bath is previously heated to 230° , the melting-point is 236° .

On acidifying an alkaline solution, and on diluting a solution in concentrated acids with water, the glucoside is not immediately precipitated if the solution is dilute. This power of remaining in a state of pseudo-solution is characteristic of saponarin, and in this condition it gives with iodine in potassium iodide the blue or violet coloration which led to its discovery. This coloration disappears on warming, but returns again on cooling. Saponarin gives with sulphuric acid a blue fluorescent solution.

Ennea-acetyl saponarin $\text{C}_{21}\text{H}_{15}\text{O}_{12}(\text{C}_2\text{H}_3\text{O})_9$, microscopic curved needles, melts at 183° – 185° . It does not give a blue coloration with iodine. When saponarin is boiled with dilute mineral acids, it is slowly hydrolysed according to the equation



with formation of glucose, *saponaretin* and a small quantity of *vitexin* identical with that obtained by Perkin (Chem. Soc. Trans. 1898, 73, 1030) from the *Vitex littoralis* (A. Cunn). According to Barger, vitexin forms pale yellow glistening plates, m.p. 260° , whereas it is described by Perkin as canary yellow needles, m.p. 264° – 265° . Molecular weight determinations carried out by the microscopic method (Barger, Chem. Soc. Trans. 1904, 85, 286; 1905, 87, 1756) indicate that the original formula $\text{C}_{15}\text{H}_{14}\text{O}_7$ assigned by Perkin to vitexin is correct (*l.c.*), rather than the second suggested formula of this latter author $\text{C}_{21}\text{H}_{20}\text{O}_{10}$.

Saponaretin $\text{C}_{15}\text{H}_{14}\text{O}_7$?, the chief product of the hydrolysis of saponarin with dilute acid consists of a light yellow amorphous powder, extremely soluble in alcohol, though in other respects it closely resembles vitexin. It may be that saponaretin is identical with Perkin's homovitexin (*l.c.*), which in the case of the *Vitex littoralis* appears to be the minor product of the hydrolysis of the glucoside there present.

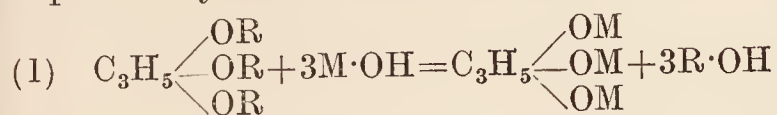
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SAPONARIN v. **SAPONARIA OFFICINALIS** (Linn.).

SAPONIFICATION. The chemical change which takes place on boiling fats with strong bases, and which results in the formation of glycerol and of salts of the higher fatty acids, has been termed 'saponification.' In a wider sense, however, every chemical process by which oil and fats are resolved into their proximate constituents—glycerol and fatty acids, is called saponification, even if no bases be used to effect the reaction.

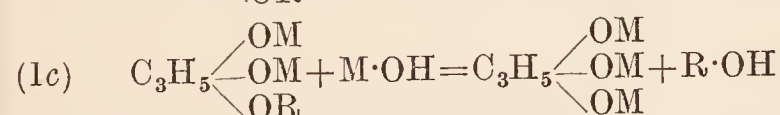
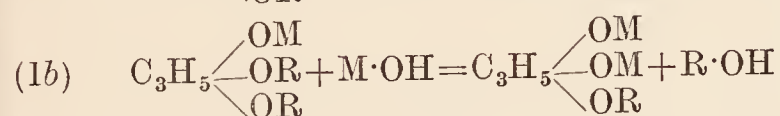
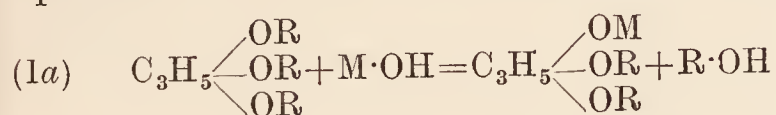
The term 'saponification' is almost exclusively used in practice, its synonym 'hydrolysis' being confined to papers of a scientific character.

The chemical change which oils and fats undergo on being hydrolysed or saponified is expressed by the following equation:—



where R denotes the radicle of any fatty acid, and M stands for hydrogen or a monovalent metal. (In the case of a bivalent metal, equation (1) must be replaced by equation (3a).)

In the light of experiments made by Geitel and by Lewkowitsch, this equation must be considered as summarising the following three equations:—



These equations express the fact that hydrolysis (saponification) takes place in three stages, the triglyceride passing through the diglyceride and the monoglyceride to the products of complete hydrolysis.

On carrying out 'hydrolysis' or 'saponification' on a practical scale, we cannot expect these three stages to take place consecutively, in distinct succession; or in other words, we cannot expect to find that the whole mass of triglycerides is at first hydrolysed exclusively to diglycerides (as indicated by the equation 1a), that the diglycerides are then broken down to monoglycerides (as shown by the equation 1b), and that finally the monoglycerides so formed are converted into glycerol and free fatty acid (1c). We shall rather find that the three phases, which are expressed by the above three equations, take place concurrently, so that at one and the same time a molecule of diglyceride may be broken down to monoglyceride and fatty acid, or a molecule of monoglyceride to glycerol and fatty acid, while a molecule of triglyceride is still intact, or is passing through the first phase. Therefore, on bringing about very rapid hydrolysis we shall not always be able to observe experimentally the intermediate transitory phases. If, however, hydrolysis or saponification be effected somewhat slowly, we are able to find in the partially saponified mass: (1) unsaponified triglyceride, (2) diglyceride, (3) monoglyceride, (4) glycerol, and (5) free fatty acid.

This has been verified to some extent by experiments of Geitel and especially by those of Lewkowitsch (J. Soc. Chem. Ind. 1898, 1107; Chem. Soc. Proc. 1899, 190; Ber. 1900, 89).

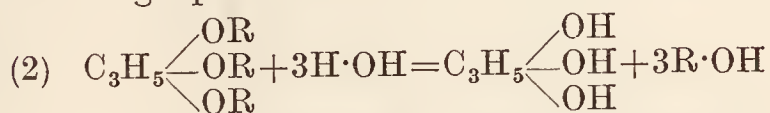
Reasoning by analogy, hydrolysis by means of sulphuric acid should also take place in stages. Direct experimental proof may be found in the observation made by Gruen and Theimer (Ber. 1907, 1801) (*cp.* also B. W. van Eldik Thieme, Koningkl. Akad. van Wetensch. Amsterdam, 1908, 855), that on hydrolysing distearo- α -chlorohydrin with 98 p.c. sulphuric acid there were obtained, in addition to still unchanged

distearochlorohydrin, the following products: monostearochlorohydrin, monochlorohydrin, and stearic acid. These products of hydrolysis thus represent the three stages of diglyceride, monoglyceride, and free fatty acid. Similarly, glyceryl trinitrate is hydrolysed by a 70 p.c. sulphuric acid to glyceryl dinitrate; and glyceryl dinitrate in its turn to mononitrate and glycerol.

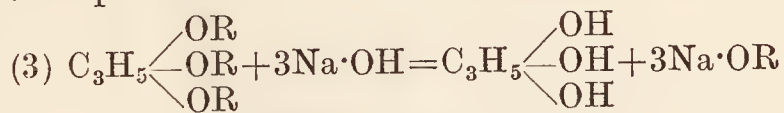
In full agreement with the foregoing is the evidence afforded by the synthesis of triglycerides, as it is possible to build them up from glycerol and fatty acid to monoglyceride, from the monoglyceride to diglyceride, and from the diglyceride to triglyceride (Berthelot).

The occurrence of dierucin (in old rape oil), for a long time looked upon as an exceptional phenomenon, is now satisfactorily explained, and the presence of mono- and diglycerides in rancid fats becomes very probable. This is well illustrated by the changes olive oil undergoes in stored olives (*see OLIVE OIL*).

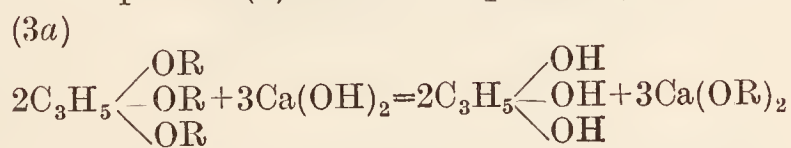
Since in the absence of water no hydrolysis can take place, water must be considered as the hydrolysing agent, whether it be employed alone, or whether its action be assisted by catalytic agents, such as acids or enzymes. In these cases the reaction is expressed by the following equation:—



If bases be chosen as catalysts (catalysers) a further chemical reaction takes place, viz. the combination of the base with the liberated fatty acids. Thus, if in equation (1) M be a monovalent metal, *e.g.* sodium, the final products will be glycerol and soda soap, as expressed by the equation—



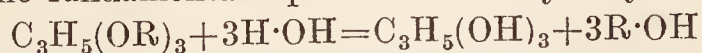
If divalent metals, such as calcium, be used then equation (3) would be replaced by (3a)—



On the reactions indicated by the foregoing equations are based the processes which are carried out on the largest scale in the fat industries, especially in the operations involving the manufacture of fatty acids and of soaps. In this article prominence must be given to the practical side of saponification; for the theoretical aspect of this question the reader is referred to Lewkowitsch, Chem. Technology, i. chap. 2.

SAPONIFICATION WITHOUT THE ASSISTANCE OF CATALYSTS.

Aqueous saponification.—The realisation of the fundamental equation of fat hydrolysis



suggests itself to the candle-maker as the ideal process. The first attempt to work such a process on an industrial scale was made by R. A. Tilghmann, whose method consisted in forcing an emulsion of fat and water through a coiled iron tube, heated in a furnace to a temperature

of about 330°. This process was, however, soon abandoned on account of the fact that hydrolysis was incomplete and considerable quantities of fatty matter were destroyed. More successful have been the modern processes of hydrolysis by means of steam at a pressure of 15 atmospheres (equivalent to about 220 lbs. per square in.) and corresponding to a temperature of about 200°. An apparatus which the author saw working on a practical scale in a Paris candle-works is the Hughes apparatus shown in Fig. 1.

The fat is introduced into the autoclave A, about 30 p.c. of water is added, and steam, generated in a multitubular boiler at a pressure sufficiently high to keep up a working pressure of 15 atmospheres in the apparatus, is admitted into the autoclave. The steam is divided into

streamlets by a distributor similar to the one shown in Fig. 3. In order to provide additional security against explosion (beyond that afforded by the safety valve) and in order to agitate the mass thoroughly, a small amount of steam is allowed to escape continuously through the pipe E, which thus serves as an additional safety valve. The escaping steam is utilised for the concentration of a glycerin solution introduced (through pipe G) into vessel B, the condensed water escaping through valve F, which acts as a kind of steam-trap. The steam evolved from the glycerin solution in B serves to pre-heat a dilute glycerin solution fed into vessel C at J. In consequence of the high temperature employed, the fatty material becomes seriously discoloured, so that the fatty acids must be chiefly

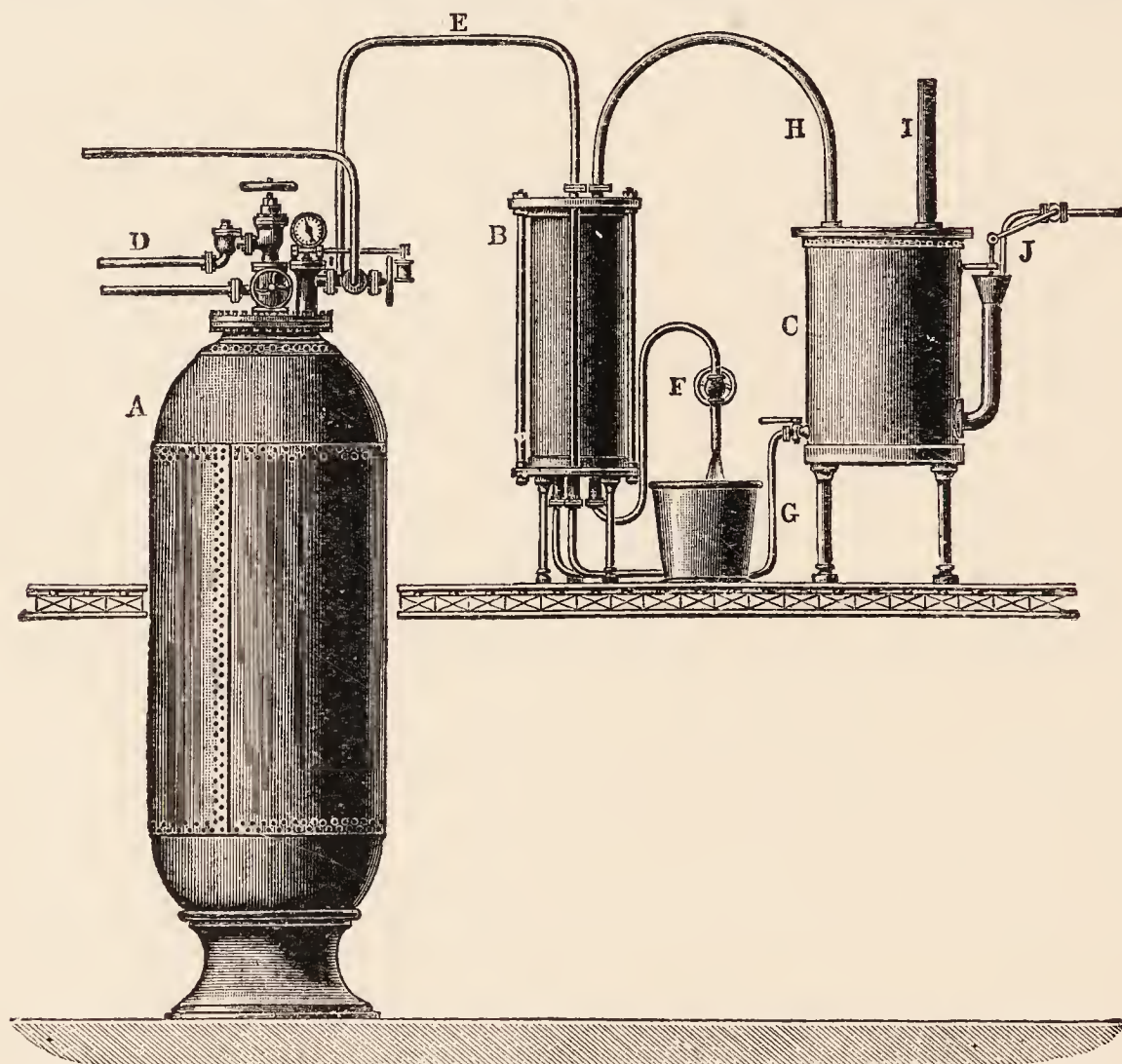


FIG. 1.

worked up by the 'mixed process' (see below). Moreover, since the hydrolysis of the fat does not reach so high a percentage as is the case in the processes described under (2), a small proportion of lime, about 1 p.c., is usually added to the mass in the autoclave. Hence, practically speaking, this method approaches very nearly those described under *Saponification with the Aid of Bases under Pressure*.

SAPONIFICATION WITH THE AID OF CATALYSTS.

It has been indicated above that catalytic agents are capable of accelerating the process of hydrolysis, in other words, that a small amount of such an agent is capable of producing hydrolysis at a more rapid rate and at a lower temperature than is employed in the case of aqueous saponification under pressure. If bases are used as accelerating agents it would therefore follow that it should not be imperative that the bases be present in at least molecular proportion

to the quantity of fatty acids that will result on complete hydrolysis. The greater the amount of the bases present the more rapidly should the resolution of the glycerides into their proximate components take place, and the greater should be the amount of salts of the fatty acids formed. But a deficiency of the bases necessary to neutralise all the fatty acids obtainable by complete hydrolysis should not preclude the completion of hydrolysis.

Since the velocity of saponification stands in direct ratio to the quantity of the bases, then, in the presence of an excess of bases, it should be possible to lower the temperature and shorten the time required for effecting practically complete hydrolysis. These views are confirmed by practice in the several modifications of the technical process of saponifying by means of lime.

1. *Saponification by means of lime in the open vat.*—The amount of caustic lime—CaO—required for a triglyceride having the mean

molecular weight 860, is according to equation (3a) 9.7 p.c., but even prolonged boiling with steam in an open vessel with that proportion of lime will not lead to complete saponification. Unless the proportion of caustic lime be raised to 12–14 p.c., the hydrolysis of the triglyceride cannot be brought to an end in an open vessel, *i.e.* at a temperature of from 100° to 105°.

The technical process based on the saponification of oils and fats by means of 12 to 14 p.c. of lime, and leading to the conversion of the total fatty acids into lime soaps, is due to De Milly. The fat is churned up with water in an open lead-lined vat by means of live steam sent into the emulsion through an open coil; while the mass is kept in ebullition, caustic lime previously slaked and made into a thin cream is gradually introduced. The boiling is maintained until the saponification is complete; this is readily recognised by the lime soap separating from the water in a curdy form. The glycerin water—'sweet water'—is then run off; the still soft lime soap is washed to remove occluded glycerol, and is then decomposed with sulphuric acid. In the older methods the lime soap was allowed to cool, when it settled as a hard mass—'rock'—from which the supernatant glycerin solution was run off. This hard lime soap was then washed, reduced to powder by grinding, and decomposed with sulphuric acid, when the calcium was precipitated as sulphate, whilst the liberated fatty acids rose to the top as a clear oily layer. The fatty acids and the glycerin—'sweet water'—are worked up for candle material (*see below*) and crude glycerin (*see GLYCERIN*).

The large amount of lime (and consequently the large amount of sulphuric acid) required in the process renders it costly, so that it has been largely superseded by methods of saponification under pressure (*see below*).

A modification of this method has been worked out by Krebitz. The saponification with lime is in principle the same as described above, with this difference, however, that the fat is not boiled with the lime until separation of the lime soap takes place, but that the water is brought into a state of complete emulsion with the oil or fat at a temperature not exceeding 100°. This emulsion is then allowed to stand overnight, when saponification takes place spontaneously, and a softish mass results which occludes the water introduced with the lime, and the glycerol formed. This mass does not offer as much difficulty in grinding as the 'rock' does. The ground lime-powder is then washed free from glycerol, when the lime soap is ready for further treatment. This process is unsuitable for candle-works. It has been introduced in some small continental soap works working up low-class bone fats, where the ground lime soap is converted into soda soap by double decomposition with sodium carbonate solution (*see SOAP*).

The process of saponification by means of lime in the open vat has, at least so far as *candle-making material* is concerned, become altogether obsolete, since a reduction of the amount of bases and acids has become imperative with a view to reduction of manufacturing costs.

2. *Saponification with the aid of bases under pressure.*—If the lime be considered a catalytic agent it should be possible, in correspondence with the views expressed above, to reduce the proportion of lime. This is actually done by carrying out the hydrolysis by means of lime in an autoclave under pressure. Under these conditions the proportion of caustic lime can be reduced gradually until, at a pressure of 12 atmospheres (corresponding to a temperature of 190°), even 1 p.c. of lime suffices for practically complete hydrolysis. Although the glyceride is, practically speaking, completely hydrolysed, only so much of the fatty acid is neutralised by lime—*i.e.* converted into lime

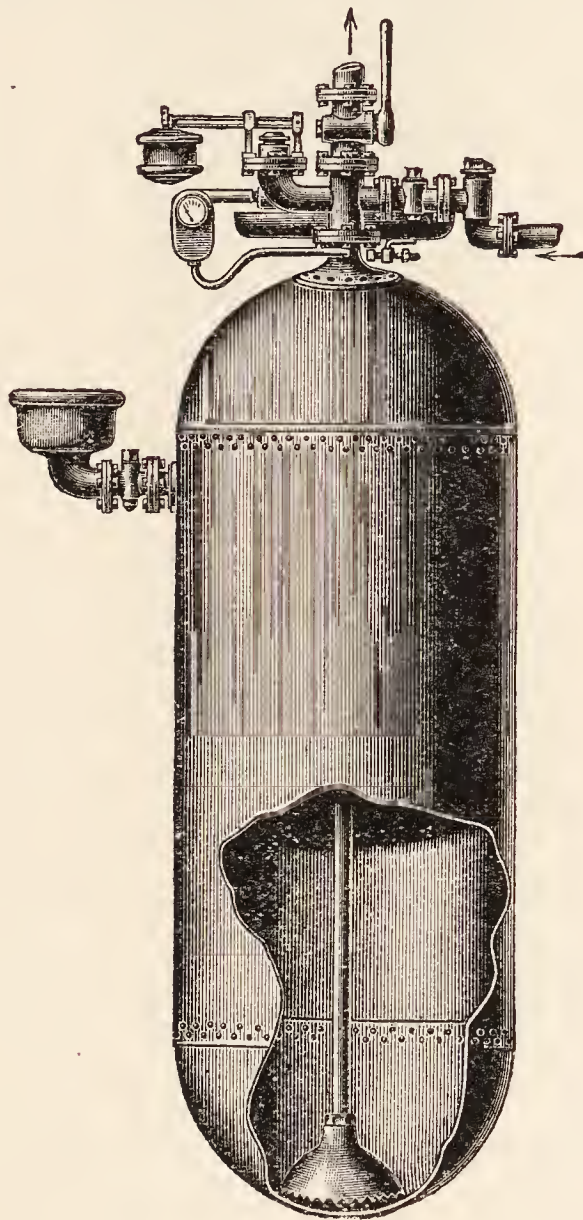


FIG. 2.

soap—as is chemically equivalent to the quantity of lime employed (*see above*).

The practice of the candle industry has, however, shown that at such high pressures the fatty acids become much discoloured; hence it has been found more advantageous to reduce the temperature, whereby an increase of the amount of catalyst required becomes necessary.

In the modern practice of *candle-works*, autoclaves are therefore worked at a pressure of about 8 atmospheres (=120 lbs. per sq. in.). At this pressure, when about 3 p.c. of lime is employed, the fat is practically completely hydrolysed. The autoclaves in use are illustrated by Figs. 2 and 3. That shown in Fig. 2 consists of a cylindrical vessel made of copper, strong enough to withstand a working pressure of 8 atmospheres, and provided with an internal steam pipe which reaches the bottom of the vessel. In Fig. 2 the steam issues from the

bottom of the serrated cone, and is thus divided into a number of streamlets which churn the mixture of fat and water into a thorough emulsion. The water and fat, in the proportion

turned on and the vessel is kept at a pressure of 8 atmospheres for about 8 to 10 hours.

The following table illustrates the hydrolysis of tallow saponified in an autoclave with 3 p.c. of lime at a pressure of 8 atmospheres.

				Free fatty acids
				per cent.
Sample taken after the	1st	hour	contained	38.55
"	"	2nd	"	77.40
"	"	3rd	"	83.9
"	"	4th	"	87.5
"	"	5th	"	88.6
"	"	6th	"	89.3
"	"	7th	"	93.0
"	"	8th	"	97.5
"	"	9th	"	98.1
"	"	10th	"	98.6

In the form of autoclave shown in Fig. 3, the agitation, effected by steam, is assisted by a mechanical stirring arrangement.

A horizontal form of autoclave fitted with a stirring arrangement of a different kind is illustrated by Fig. 4.

Since cylindrical autoclaves if not sufficiently strong are liable to be bulged out by the high pressure, they would at last, if the bulging took place progressively in a regular manner, assume the shape of a sphere. Hence spherical autoclaves (first suggested by L. Bottaro of Genoa) are also in vogue. An autoclave of this kind, provided with a stirring arrangement, is shown in Fig. 5.

In the processes considered here the hydrolysis reaches as high a figure as 98 to 99 p.c. If the temperature, time and amount of reagent be reduced, the hydrolysis may not reach so high a degree and may only amount to 96 to 97 p.c.

For the purposes of the candle industry, such discoloration as the fatty acids unavoidably undergo in this process is of little account, as the colouring bodies can be easily removed by subsequent treatment. Since, however, attempts have been made to apply this process of hydrolysis to fats intended for soap-making (*see SOAP*), it was found necessary

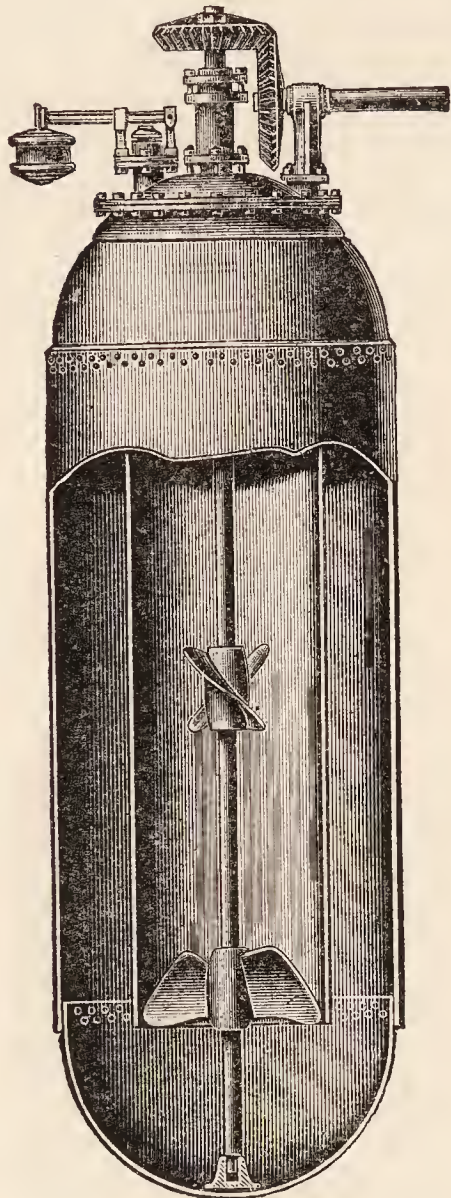


FIG. 3.

of 1 to 3, or 1 to 4, as also the milk of lime, are introduced through the funnel-shaped vessel at the side of the autoclave.

When the autoclave is charged, steam is

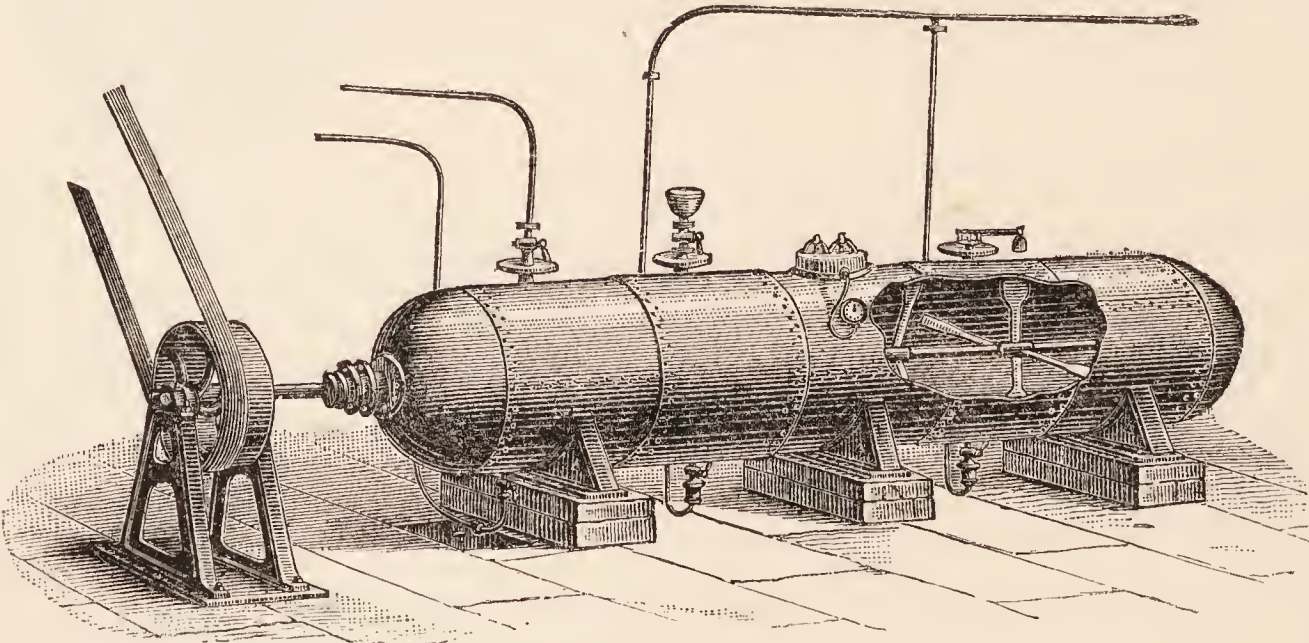


FIG. 4.

still further to reduce the temperature, and the autoclaves are therefore worked for this purpose at a pressure of 5 to 6 atmospheres only. This feature (intensified by an attempt to reduce the proportion of bases) leads to a reduction of the proportion of fat undergoing hydrolysis;

hence, in the practice of preparing fatty acids for purposes of soap-making no higher amount of hydrolysis than about 80 p.c. is reached. Even at this pressure serious discoloration of the fatty acids takes place (*see SOAP*). The technical operation is conducted practically in the same

manner as described under *Aqueous saponification*.

When the saponification is deemed complete, the saponified mass is allowed to stand in the autoclave until it has separated into two layers: glycerin water—'sweet water'—and an upper layer of fatty acids, containing as much lime soap as corresponds with the lime introduced into the autoclave. These two layers are either pumped separately into store vats or the whole mass may be pumped into a settling vat, where the separation into two layers takes place. The further working up of the glycerin solution into 'crude saponification glycerin' has been described under GLYCERIN. The fatty layer is boiled up with steam, and sufficient sulphuric acid is added to decompose the lime soap. On allowing the mixture to stand, most of the calcium sulphate separates out at the bottom of the aqueous layer, whereas the fatty acids form a clear oily layer on the top. They are washed

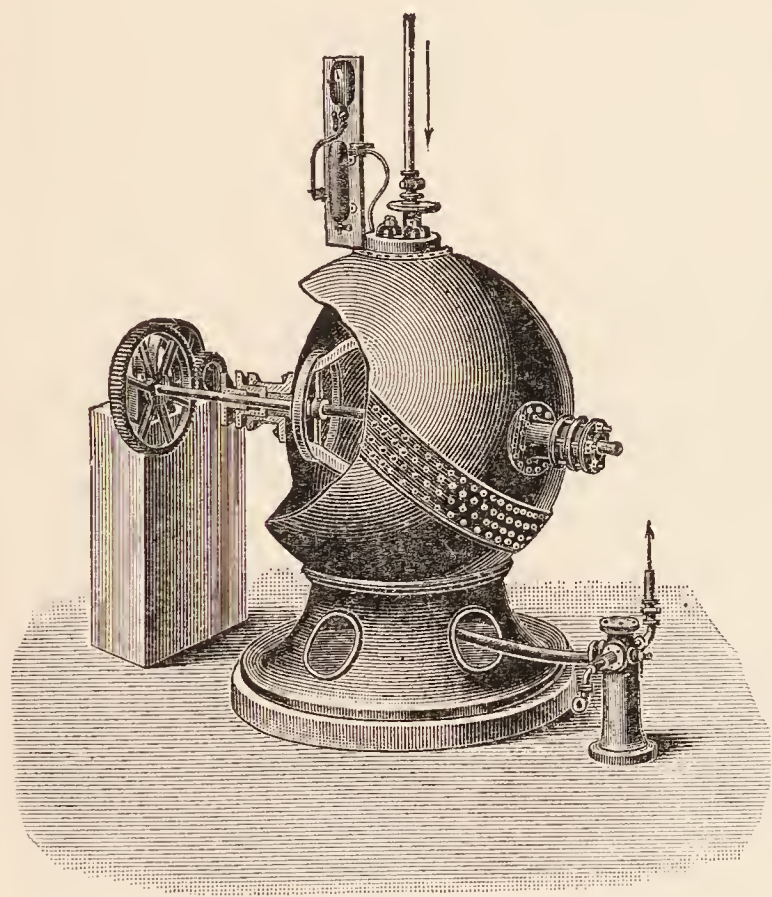


FIG. 5.

carefully with dilute acid to remove the last traces of lime. Some manufacturers precipitate the lime in the last stages as oxalate.

In place of lime, magnesia and zinc oxide (to which latter zinc-dust is also added), are employed as 'accelerators.' The advantage offered by magnesia and zinc oxide consists in the fact that they do not yield a precipitate on decomposing the autoclaved fatty matter with sulphuric acid. This advantage is, however, counterbalanced by the fact that hydrolysis is not so readily effected by means of magnesia, at any rate in the case of tallow and palm oil, as by means of lime. Experience gained on a large scale has shown that tallow, autoclaved with 3 p.c. of magnesia under the same conditions as with 3 p.c. of lime, is hydrolysed only to the extent of about 96 p.c. In order to reach as good a result as is obtained by means of lime, the working pressure or (and) the length of time must be increased. This is borne out by the following table:—

SAPONIFICATION OF SHEA BUTTER WITH 3 PER CENT. OF MAGNESIA AT A PRESSURE OF 9 ATMOSPHERES.

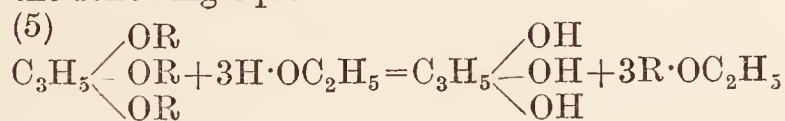
			Free fatty acids, per cent.	
Sample taken after the	1st hour	contained	61.4	63.2
"	"	2nd "	80.2	81.9
"	"	3rd "	90.2	90.1
"	"	4th "	91.1	94.8
"	"	5th "	95.4	95.7
"	"	6th "	95.5	97.1
"	"	7th "	96.6	97.1
"	"	8th "	98.1	98.0

The pressure being higher than in the case of lime, discoloration of the fatty acid takes place to a somewhat greater extent, and the resulting 'sweet water' is more dilute. The chief disadvantages of magnesia lie, however, in the fact that it frequently forms emulsions, which are very troublesome, as they do not separate even after prolonged standing, and, as pointed out already, that the saponification is less complete.

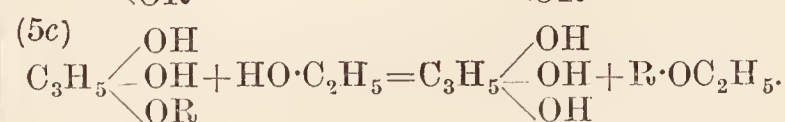
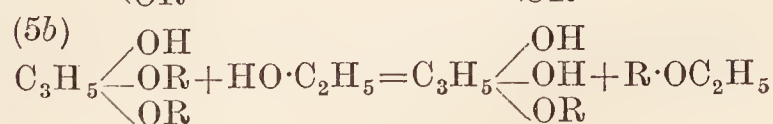
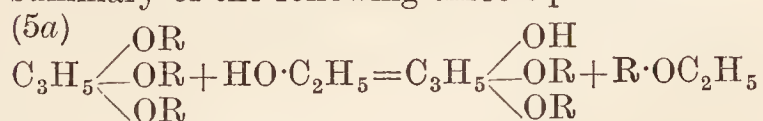
Zinc oxide does not offer these disadvantages, but its higher cost outweighs the benefit derived from its use. A small percentage of zinc oxide or zinc-dust is, however, frequently used conjointly with lime, as the discoloration of the fatty acids is thereby somewhat diminished.

3. *Saponification by means of caustic alkalis.*—There can be no doubt that under pressure, complete hydrolysis would be brought about by an amount of caustic alkali insufficient to neutralise all the fatty acids formed. On a large scale, for obvious reasons, such a process is not employed. The compounds resulting from the combination of fatty acids and caustic alkalis being useful commercial products—soaps—the aim of the manufacturer is to conduct operations so that these products are obtained concurrently with the hydrolysis of the fats. Hence, on a commercial scale oils and fats are boiled in open vessels with a solution of caustic alkalis, containing not only sufficient alkali to neutralise all the fatty acids obtainable on hydrolysing the glycerides, but also an excess, whereby the time required for the completion of the reaction is shortened. Indeed, this excess of alkali is required in order to carry out the reaction in the shortest possible time (*see SOAP*).

The laboratory method of saponifying fats by means of alcoholic caustic potash or caustic soda (*see OILS, FIXED, AND FATS*) need not be considered as differing, theoretically, from hydrolysis in aqueous solutions, if we look upon alcohol as water in which one hydrogen atom is replaced by the group C_2H_5 . Ignoring for a moment the alkali, hydrolysis would proceed according to the following equation:



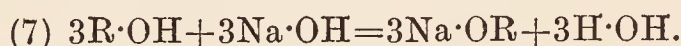
which should, again, be looked upon as a summary of the following three equations:



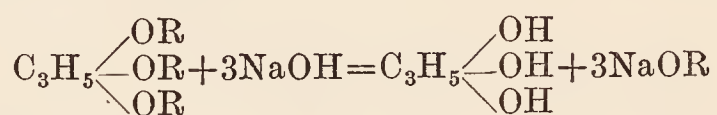
The resulting products would be glycerol and the ethylic esters of the fatty acids. Although the feasibility of those reactions had not been tested experimentally, the author (J. Soc. Chem. Ind. 1903, 595) had expressed the opinion that with anhydrous materials and under high pressure, especially if assisted by a suitable catalyst, the reaction would very likely proceed a long way in the direction indicated by the equation (5).

In the absence of water the chemical change cannot proceed beyond the formation of ethyl-esters. But if the alcohol contain water, the ethyl-esters in their turn are hydrolysed by the water to some extent. Complete hydrolysis, such as indicated by the following equation:

(6) $3C_2H_5 \cdot OR + 3H \cdot OH = 3R \cdot OH + 3C_2H_5 \cdot OH$, cannot result, since an equilibrium between ester, water, and free fatty acids would soon be established. The reaction thus arrested will, however, proceed, if alkali be present, to neutralise the free acid formed. Since in laboratory operations caustic alkali is added to the alcohol in quantity greater than that which is chemically equivalent to the fatty acids, the fatty acids formed (equation 6) will be immediately neutralised, as is illustrated by the following equation:



Hence, the chemical change represented by equation (6) will become complete. By adding the three equations (5, 6, and 7), we obtain as the final result



which is identical with equation (3) given above.

For further explanation dealing with the mechanism of saponification in alcoholic solution and the action of sodium ethylate, *cp.* Lewkowitsch, Chem. Technology, i.

4. *Saponification by means of ammonia.*—Ammonia is also capable of acting as an accelerating agent in the hydrolysis of oils and fats, and has therefore been frequently suggested as a saponifying agent. The properties of ammonia render it imperative to carry out the hydrolysis under pressure, and several special autoclaves have been patented for this purpose. None of these suggestions has found practical application. Barbé, Garelli, and de Paoli claim that in their process (protected by French Patent 372431 and 1st Add. No. 9255), the total amount of ammonia is recovered by treating the ammonia soap formed in a current of steam.

5. *Saponification by means of acids.*—Since, as in the case of many chemical reactions, acids act as catalysts, it is possible to employ them to accelerate the hydrolysis effected by water.

(a) *Saponification by means of hydrochloric acid.*—The author (J. Soc. Chem. Ind. 1903, 67) has shown that oils and fats can be hydrolysed by means of hydrochloric acid, sp.gr. 1.16. As this method has not yet acquired practical importance, it need only be pointed out here that hydrolysis becomes much slower after about 75 p.c. of the neutral fats has been hydrolysed. The fact that under the conditions of the experiments it was very difficult to keep up a thorough intermixture of fat and acidulated

water, satisfactorily explains this slowing down of the reaction. It may be safely assumed that provided a thorough intermixture, as in an emulsion, could be brought about, hydrolysis would proceed much more rapidly, for the catalytic action of hydrochloric acid takes place even at the ordinary temperature, provided sufficient length of time be allowed, as has been proved by experiments.

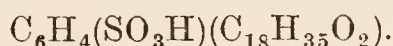
(b) *Saponification by means of concentrated sulphuric acid.*—Much better results are obtained by employing as a catalyst *concentrated sulphuric acid*, which seems to act to some extent as an emulsifying agent in the *technical process of hydrolysis by means of concentrated sulphuric acid*. The action of sulphuric acid, first described by Cornett in 1777, consists, in the first instance, in the formation of sulpho-compounds of glycerides, the composition of which has been investigated by Geitel (J. pr. Chem. 1888, 37, 53; *cf.* Lewkowitsch, J. Soc. Chem. Ind. 1897, 392).

The technical operation consists in rapidly intermixing fat which has previously been heated to a temperature of 120° or more (and thereby freed from the last traces of moisture) with 4–6 p.c. of concentrated sulphuric acid of 66°–67°Bé. If sulphuric acid of lower strength be used the hydrolysis is not complete (*cf.* Lewkowitsch, Chem. Tech. of Oils, &c., i.). With the decrease in the strength of sulphuric acid hydrolysis decreases rapidly; an acid of 60 p.c. SO_4H_2 is no longer capable of effecting hydrolysis on a practical scale. The behaviour of sulphuric acid towards the saturated glycerides is of little practical importance, since sulphonated compounds (of the glycerides as well as of the saturated fatty acids) that are formed are subsequently decomposed, yielding the original saturated acids practically unchanged. With olein, however (less saturated glycerides than olein need not be considered here, as being of no practical importance in the manufacture of 'stearine'), the sulphuric acid forms saturated sulphonated compounds, a small quantity of sulphurous acid being at the same time evolved in consequence of secondary reactions. These sulphonated compounds have the property of being somewhat readily hydrolysed on boiling with water. The chemical change will be referred to below; here it may suffice to state that from 15 to 17 p.c. of oleic acid is converted into solid products, chiefly stearylactone and isomeric solid oleic acids ('isoöleic acid,' see OILS, FIXED, AND FATS) with which small quantities of hydroxy acids may be admixed.

The higher the temperature to which the fat has been heated and the larger the percentage of sulphuric acid used, the more copious is the evolution of sulphurous acid and the further will the secondary reactions proceed. In order to reduce the destruction ('carbonising') of organic matter, which necessarily leads to a lower yield of fatty acids, and especially of glycerin, great attention must be paid to the following factors: quantity of sulphuric acid, temperature, and time during which the acid is allowed to act on the fat. In order to ensure the most intimate contact of the fat with the acid within the shortest possible time, various mixing machines are used. Mixing by means

of air cannot be recommended, as this leads to deterioration of the material and to appreciable losses. One type of apparatus is shown in Fig. 6. Other devices consist of pulverising the fatty matter by centrifugal force, &c.

(c) *Saponification by means of sulpho-aromatic compounds.* A much more pronounced emulsifying action than that produced by concentrated sulphuric acid is obtained by the sulpho-aromatic compound invented by Twitchell (U.S. Pat. 601603 of 1897). The reagent employed in this process is obtained by allowing an excess of sulphuric acid to act on a solution of oleic acid in aromatic hydrocarbons. The product obtained in case benzene is chosen as the aromatic hydrocarbon has been described by Twitchell as having the composition



The composition of the reagent as actually supplied to the licensees under the name of 'saponifier' is kept secret. The author does not,

therefore, feel justified in making detailed statements as to the manner in which it is prepared for manufacturing purposes beyond pointing out that the aromatic hydrocarbon in the 'saponifier' is naphthalene.

The rationale of this process is not yet fully understood. The present author explained the action of the reagent by its power of emulsifying the glycerides and has shown that the same emulsifying action is produced by reagents prepared from anthracene and phenanthrene (cf. Lewkowitsch, Chem. Tech. i.). The 'Twitchell process' differs most essentially from the 'acid saponification process,' in that oleic acid is not simultaneously converted into solid material; hence the fatty acids obtained by this process have the same composition as those yielded by the autoclave process. This last-mentioned fact would seem to prove that true sulphonated acids have not been formed; moreover, it has been shown above that dilute sulphuric acid does not produce hydrolysis.

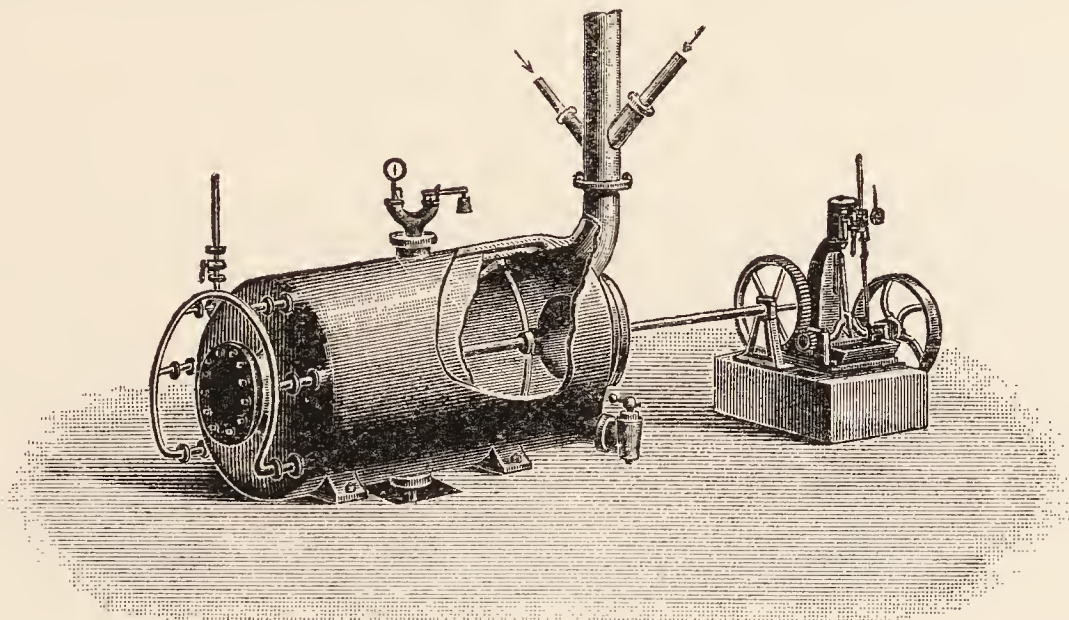


FIG. 6.

It is essential that the fatty material to be treated by this process be freed from impurities, such as lime, iron, as also from foreign organic substances. This is done by boiling the fat with a dilute solution of sulphuric acid. The purified fat is then transferred to wooden vessels furnished with perforated brass coils and provided with well-fitting lids, which allow the steam to escape but prevent free access of air, since the fatty acids formed in this process readily darken on coming into contact with air. In these vessels the fat is mixed with 50 p.c. of its weight of distilled water, 1.5 to 2 p.c. of the reagent are then added, and the whole mass is agitated by open steam passing through the perforated coil. It is essential that the fatty matter contain at the outset a small proportion of free fatty acids, as an entirely neutral fat requires a somewhat lengthy time before hydrolysis commences. This is no doubt due to the fact that the aqueous solution of the reagent requires the presence of fatty acids, in order to produce an emulsion which is essential for the progress of hydrolysis. With neutral fats a somewhat longer time is required to start the hydrolysis, as free fatty acids must be produced first by the boiling with water. But even at best the process requires a considerable time for the practical completion of hydrolysis.

For the purposes of the candle-maker it is essential that the hydrolysis be as complete as possible; practically complete hydrolysis can be reached by prolonged boiling. The emulsion is then 'broken' by the addition of sulphuric acid of 60°Bé., and the contents of the vessels are allowed to settle, when separation into two layers takes place—an upper layer of fatty acids, and a lower aqueous one containing glycerin. The fatty acids are drawn off and washed, and are ready for subsequent treatment.

For the working up of the glycerin, see *Crude Glycerin from the Twitchell Process* under GLYCERIN.

In a process claimed as an improvement on the original Twitchell method (Eng. Pat. 749 of 1912), the fats or fatty acids are hydrogenated prior to the sulphonation, with the object of obtaining a product of a lighter colour. For example, 100 parts of castor oil are hydrogenated and mixed with 100 parts of naphthalene, and the mixture is gradually treated with sulphuric acid of 66°Bé. at a temperature below 20°. The mass is poured into 800 parts of water, and the upper layer which separates is filtered and used as the catalytic agent.

In Petrow's process (Eng. Pat. 27244 of 1911) the catalytic agent consists of the sulphonated acids or other compounds obtained

by treating petroleum oils with sulphuric acid, whilst in a later patent (Eng. Pat. 17148 of 1914) the hydrolytic agent is prepared by sulphonating hydrocarbon oils derived from coal tar, lignite tar, peat tar, or bituminous minerals. It is known commercially as the 'Kontakt reagent,' and is used in the same way as Twitchell's reagent.

6. *Saponification by means of enzymes.*—The explanation of the rationale of the Twitchell process attempted above would seem to show that the action of the reagent is purely catalytic without any secondary reactions taking place, and resembles the action of enzymes which accelerate hydrolysis without apparently undergoing any chemical change. The action of enzymes as conditioning the initial stages of rancidity by effecting hydrolysis has been explained in the article OILS, FIXED, AND FATS.

Connstein, Hoyer, and Wartenberg showed that the enzyme contained in castor seed is capable of accelerating the hydrolysis of triglycerides to such a considerable extent that a technical process of saponification can be based on the action of the castor seed ferment.

The original *modus operandi*, in which ground castor seeds (together with their husks) were brought into an emulsion with oils (or fats) and water, slightly acidulated with acetic acid or acid salts, has been abandoned, as the formation of a most troublesome middle layer between the fatty and aqueous layers led to considerable losses of fatty matter and other concomitant drawbacks (low quality of glycerin, &c.). Even the use of decorticated seeds, although palliating the evil, did not remedy the inconveniences. The author's suggestion, viz. to isolate the enzyme itself, has been worked out into a manufacturing process by Nicloux, who triturates decorticated castor seeds with castor or cotton seed oil, filters the mass through a fine silk gauze, and separates by means of centrifugal force the turbid oil so obtained. The residue remaining on the filter may be subjected again to the same process, but in practice it is thrown away as valueless. The turbid filtrate separates into three layers. The excess of oil forms the uppermost layer, the practically inactive aleurone grains and membranes fall to the bottom, whilst the cytoplasm, emulsified in oil, is found in the middle layer. This latter is used as the hydrolysing agent.

Hoyer also endeavoured to isolate the enzyme, or at least to obtain preparations richer in active substance than the castor seeds themselves. Hoyer insisted on the necessity of working in an acid medium, but Nicloux found that the best technical results were obtained in a neutral medium (*e.g.* a solution of magnesium and calcium sulphates), and that it was advantageous, especially in the case of oils and fats containing glycerides of lower fatty acids, to remove the free acids by washing with soda. The retarding effect of lower fatty acids was confirmed by Hoyer, who found that the castor seeds contained acid-forming water-soluble ferment, which produced sufficient acid to 'activate' the lipolytic enzyme (Nicloux's 'lipaseidin'), and which seems to consist of a mixture of volatile fatty acids and lactic acid. A series of experiments undertaken by Hoyer with a view to isolating the lipolytic enzyme

by means of a mixture of light petroleum and chloroform led to the preparation of 'ferment-oil,' consisting of a mixture of castor oil and protoplasma (Nicloux's cytoplasma), and forming about 64 p.c. of the original castor seed.

This 'ferment-oil' has been replaced by the preparation 'ferment-milk' (termed in technical practice 'ferment'). The 'ferment' is obtained in the following manner: Decorticated castor seeds are ground up with a large quantity of water in a suitable mill, and the mass is filtered from the suspended solid substances, whereby a white creamy liquor is obtained. If this liquor is allowed to ferment spontaneously, water separates, and there rises to the top a thick creamy emulsion, consisting of 38 p.c. of castor oil fatty acids, 58 p.c. of water, and 4 p.c. of proteins. The latter constitute the actual lipolytic agent. Finally, it was found that a better 'activator' than magnesium or calcium sulphate is manganese sulphate, the addition of which to the emulsion has also been patented. (The accelerating action of certain metallic salts was discovered by Pottevin.) In the manufacturing process oil or fat is introduced into a lead-lined vessel having a conical bottom, and provided with a steam-heating coil and a perforated coil for supplying compressed air. With the aid of the air current an emulsion is produced, whilst about 40 p.c. water, 5 to 8 p.c. of the 'ferment,' and 0.2 p.c. of manganese sulphate is introduced. After intermixture has been effected, the mass is allowed to stand for one or two or more days, according to the required amount of hydrolysis. During the first hours, the mixture must be observed carefully, as separation of the emulsified mass may occur. By stirring afresh, the emulsified state can be re-established, when the enzyme begins to exert its action. When the desired degree of hydrolysis is reached the mass is warmed at 80°–85°, and 0.3 to 0.45 p.c. (reckoned on the fatty material) of a 50 p.c. sulphuric acid is introduced, while the mass is stirred (by air). The steam is then turned off, and the contents of the vessel are allowed to settle. The mass separates into three layers: (1) an aqueous layer at the bottom, containing glycerin; (2) a clear layer of fatty matter on the top; and (3) between these two a middle layer consisting of an emulsion of proteins, glycerin, fatty matter, and water. This middle layer is allowed to accumulate, and by warming and renewed treatment with water a further separation into three layers can be effected, so that the loss incurred by the formation of this middle layer may be reduced to the smallest possible amount. If the mass has been allowed to rest in the emulsified state for 24 hours, the fatty matter contains, as a rule, about 80 p.c. of free fatty acids. By allowing the enzyme to act for 24 hours longer, a further 10 p.c. of neutral fat may be hydrolysed.

It is very important to ascertain for each individual oil or fat that temperature which is most suitable for it, and to maintain this while hydrolysis takes place. It is not advisable to allow the temperature to fall below 10°, and it is best to work at 2° or 3° above the melting-point of the fat. As the cytoplasm is readily destroyed when heated to 42° in contact with water, it is obvious that tallow is not a suitable material to be hydrolysed by this process, and

it is difficult to obtain a product containing 75 p.c. of free fatty acids from a low-melting tallow, whilst high-melting tallows are not workable on a large scale. The hydrolysis of tallow can, however, be effected, if it be mixed with suitable oils or fats so as to reduce the melting-point of the mixture to below 35°.

The enzyme must be used in as fresh a state as possible. The author observed that after a few days' standing the lipolytic power becomes greatly reduced. This would be readily explained by the fact, observed by Hoyer, that the 'ferment' is much more easily affected (injuriously) by acids than is the original castor seed pulp.

The glycerin obtained by this process has been described under *Fermentation Crude Glycerin* (see GLYCERIN).

With the exception of the ammonia process No. 4 and process No. 1, all the above described processes are employed on the largest scale in the candle and soap industries, as has been mentioned already incidentally. It need, therefore, only be briefly repeated that the processes enumerated under Nos. 2 and 5*b* and to a very

small extent No. 5*c*, form the basis of the *stearine candle industry*, whereas the processes mentioned under Nos. 3 and 6 are practised in the *soap industry*. Process No. 5 is carried out on an immense scale, whereas No. 6 occupies only a very unimportant position in the soap industry. Of recent years autoclave processes have been also introduced into soap works (see SOAP).

Here we only deal with the working-up of the fatty matter, obtained after the removal of the glycerin in *candle works*.

AUTOCLAVE PROCESS.

According to the fatty material employed, the composition of the resulting fatty acids will naturally vary. The chief materials employed hitherto, at any rate in this country in the saponification processes (2), (5*b*) and (5*c*) described above, are tallow and palm oil, or a mixture of both; hence it may be taken that the fatty acids consist approximately of 50 p.c. of solid acids and 50 p.c. of oleic acid. Bone fat, especially on the Continent, is also largely 'autoclaved' for candle-making purposes. The

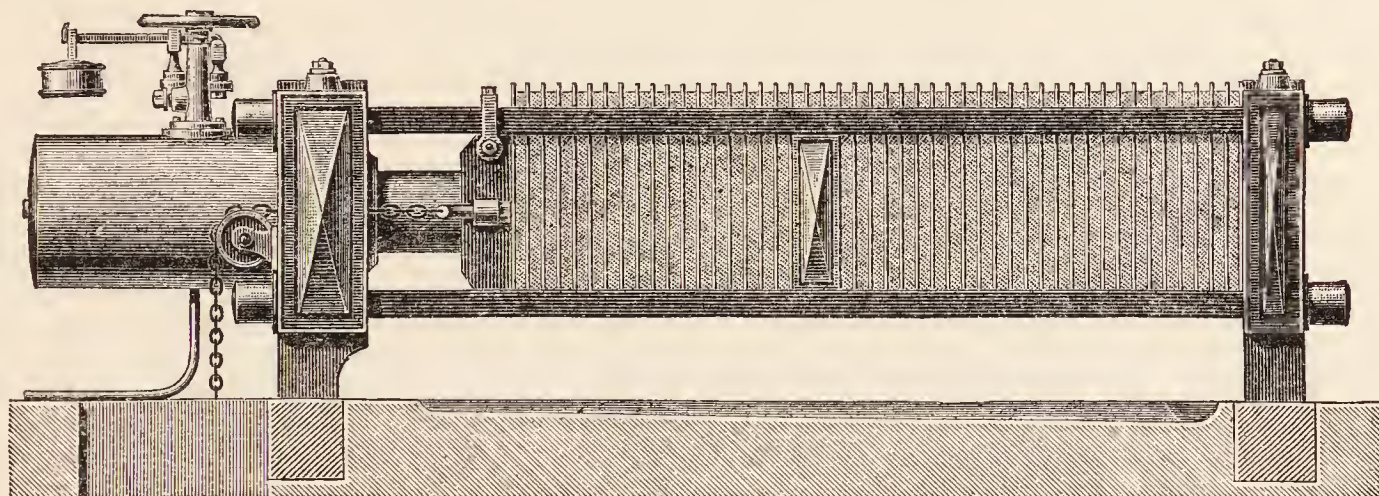


FIG. 7.

kind of bone-fat employed for this purpose is the benzine-extracted, which is unsuitable for soap-making purposes. Since candles made exclusively from bone fat stearine are soft and friable, it is customary to make up the charges for the autoclave from a mixture of bone fat and other fats. With regard to goat's tallow as a candle material, see Lewkowitch, ii.

'Cotton seed stearine' of a high 'titer' test—above 40°—is also used to some extent as a raw material for candle-making purposes.

In the United States such lard stearine as is unfit for edible purposes is not infrequently converted into candle material by the autoclave process. A sample of such material examined in the author's laboratory had the melting-point 51.7°.

The employment of palm oil is somewhat restricted on the Continent, and other vegetable fats—such as vegetable tallow, shea butter, mowrah seed oil—are in use. The commercial exploitation of the large supplies of vegetable fats suitable for the candle industry has not yet, however, attracted as much attention from importers as this subject deserves.

Since oleic acid is useless as a candle material, the next operation, after washing the crude fatty acids free from mineral acid, is to effect its removal from the mixed fatty acids. Hitherto

this has been principally done by pressing the mixed fatty acids. The crude acids are run into shallow trays arranged in tiers, in which the fatty acids are allowed to crystallise. These trays are best placed in a room which can be kept at any desired low temperature; hence this room is fitted with cooling coils fed with cold brine from a refrigerating plant. The temperature at which the crystallisation takes place is carefully regulated, so as to obtain well-formed crystals of stearic and palmitic acids embedded in the mother-liquor of oleic acid. If the fatty acids are cooled too rapidly, they solidify to an amorphous mass from which it is extremely difficult to express the oleic acid satisfactorily (*i.e.* the mass 'spues'). The solidified mass is taken out of the trays and pressed, at first at the ordinary temperature in a cold press, such as is shown in Fig. 7. The bulk of the oleic acid—'red oil'—is thereby removed. The hard cakes still contain too much oleic acid, and are therefore pressed a second time, at a somewhat higher temperature, in a hot press (Fig. 8), the cakes being placed in a bag of horse-hair or other suitable material, between press plates heated by live steam. In the figure shown, the steam is supplied from above; but since the stuffing-boxes, owing to the wear and tear to which they are subjected, require frequent

renewing, the steam is supplied in more modern presses from below.

The cakes are allowed to stand under pressure when heated until a sufficient amount of oleic acid has been expressed to leave them white, ready to be melted (after a further purification to remove the last traces of lime)

and to be moulded into candles. The oleic acid which runs from the hot-pressed cakes contains a considerable amount of solid acids ('stearine'). They are recovered either by adding the material to a fresh batch of the original fatty acids, or by subjecting it, together with the 'red oil,' to a process of cooling in a refrigerating house.

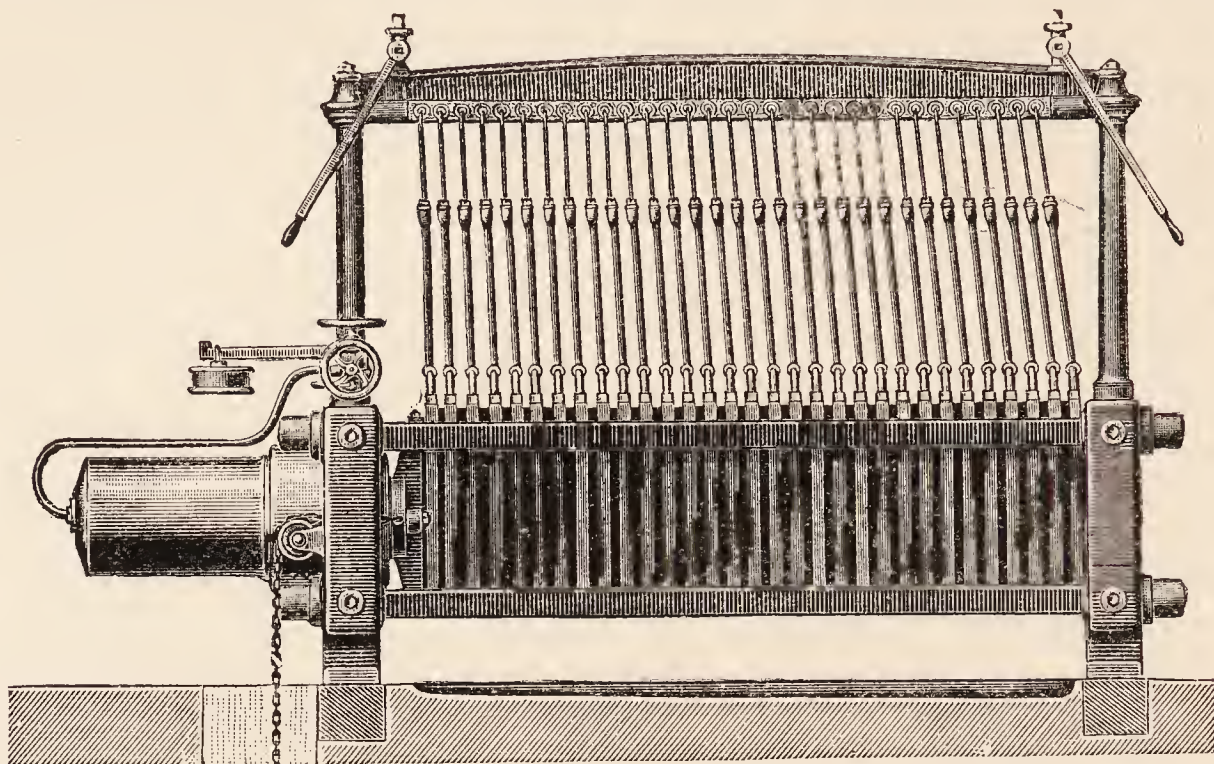


FIG. 8.

If the 'stearine' is not sufficiently white, the mixed fatty acids are subjected to distillation, previous to being pressed. For a method patented by Lanza for separating oleic acid from the solid acids by means of a dilute solution of stearo-sulphuric acid, *cp.* Lewkowitsch, Chem. Tech. iii.

The 'stearine' contained in the 'red oil' (and in the runnings from the hot press) is recovered in the refrigerating house by cooling the liquid mass. Various appliances are in vogue. The simplest plan is to refrigerate the oil in large tanks fitted with a row of coils through which cooled brine or calcium chloride solution is pumped. Some manufacturers cool small quantities in mixing vessels, so as to be able to stir the cooled mass. The process requires attention, as the success of the operation depends on the separation of well-formed crystals. These are readily separated from the oleic acid by means of a filter-press.

A more rapid method of cooling consists in allowing the red oil to run over a refrigerating wheel—Petit's wheel (Fig. 9). This wheel is shown partly in section. The cooled brine enters at *c*, runs along the circumference of the wheel, and leaves it at the opposite side. The oleine is run into trough *f*, into which dips the rotating wheel, carrying with it upwards a thin film of oleic acid, which is thus rapidly cooled and deposits crystals of 'stearine.' The crystalline mass on reaching the scraper *h* is scraped off and the sludgy mass is collected in the cooled vessel *r*, from which it is pumped through pump *p* into a filter-press. The crystals form an intermediate product, and are mixed with the crude candle material at a suitable stage of the process.

The yield of candle material by the *autoclave process* depends, of course, on the melting-points

of the finished 'stearine,' and on the completeness with which the 'stearine' is recovered from the 'red oil.' It may, however, be taken as sufficiently accurate that the amount of high melting 'stearine' from tallow or palm oil, or a mixture of both, varies from 45 to 47 p.c. of the raw material, about 30 p.c. being obtained from

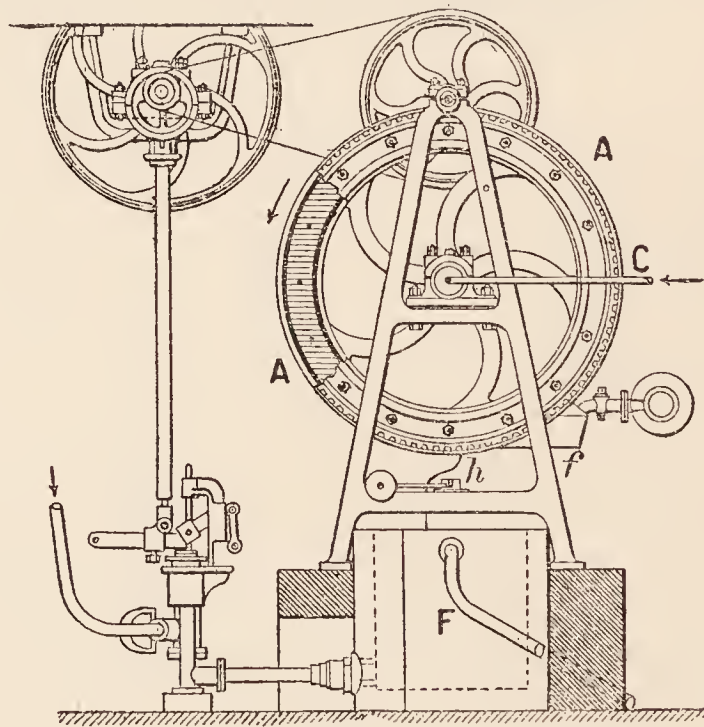


FIG. 9.

the hot press and the remainder from the refrigerated 'red oil.' The proportion of finished oleic acid, 'oleine,' amounts to 47-48 p.c. In the case of good tallow, the yield of saponification crude glycerin of sp.gr. 1.240 reaches 10 p.c.

The 'stearine' is used as candle material either as such, or in admixture with paraffin wax, &c. (*see CANDLES*). The oleic acid, 'oleine,' is either converted into textile soap or used as a

wool oil (*q.v.*). In the 'mixed process' (see below) part of the oleic acid is converted into 'candle material.'

If the fatty acids obtained by the autoclave process be too dark, and hence do not yield a sufficiently white candle material, they must be purified by distillation (see below). This is carried out in the apparatus described under *Acid saponification*.

During the distilling process the fatty acids do not undergo a chemical change, provided due care be observed in conducting the distillation. Since, however, the 'autoclaved' mass contains some small proportions of unsaponified fat, which goes on accumulating in the still—especially if the still be fed continuously—decomposition of the unsaponified fat finally takes place with formation of hydrocarbons, which are produced somewhat rapidly when the accumulated neutral fat amounts to 12–15 p.c. of the still contents.

ACID SAPONIFICATION PROCESS.

The further working up of the sulphonated mass as obtained in process 5b is as follows:—

The sulphonated mass is run into boiling water and agitated by steam until the sulphonated compounds are hydrolysed. On standing, separation into two layers takes place: a lower aqueous layer containing the sulphuric acid employed and also the glycerol, and an upper layer of fatty material.

This fatty material is, as a rule, so dark that it cannot be worked up by pressing immediately after solidifying, in the manner described below. In order to obtain material of good colour the fatty mass must be distilled. A type of apparatus employed for this purpose is illustrated by Fig. 10. The fatty material, thoroughly freed from mineral acid by washing with water, is introduced into still A, where it is heated at first by direct fire. When the material

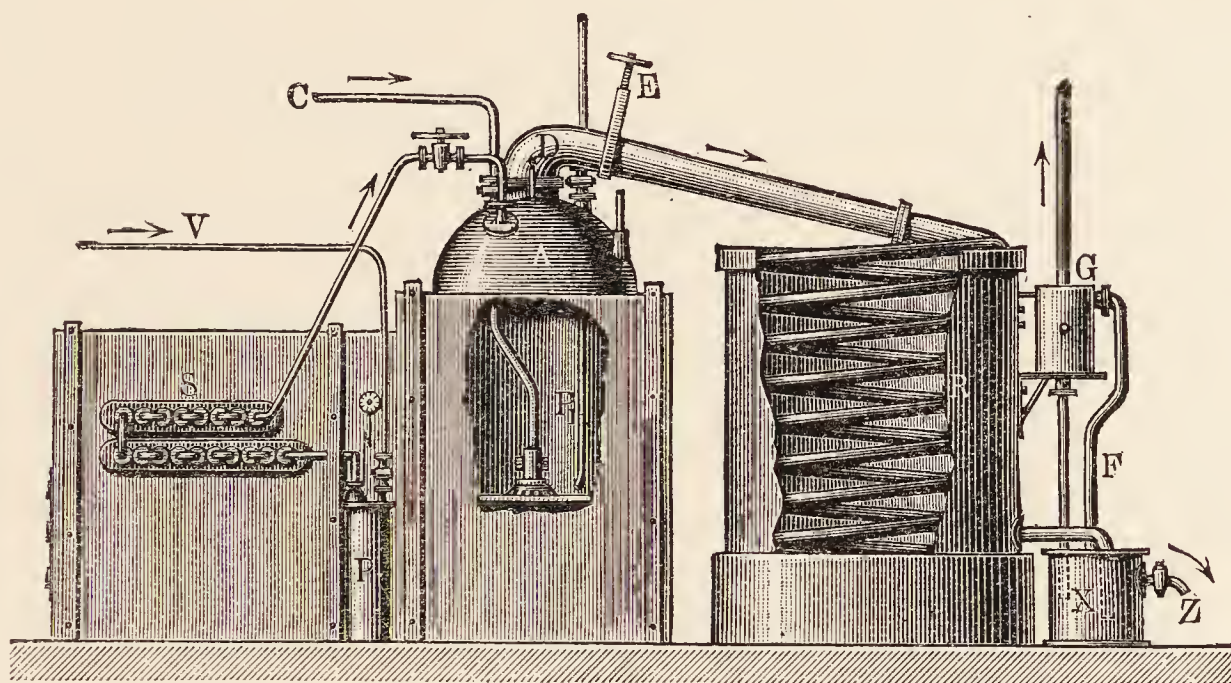


FIG. 10.

is sufficiently hot, a current of steam, dried preliminarily in P and superheated in S, is introduced through P₁, and the fatty acids are thus carried over through D, into the cooling worm R. The acids and the condensed water run into box X, where their separation takes place, and any vapours escape through G. The fatty material which is drawn off at Z, represents a mixture of liquid acids and candle material, which is pressed in the cold and subsequently when hot as described above. A large number of patents have been taken for special forms of stills and for processes claiming continuous feeding, distillation *in vacuo*, or both combined. Stills of the ovoid form shown in Fig. 10 have been largely replaced by stills of lenticular shape. In order to reduce the height to which the vaporised fatty acids must rise, the condensing arrangements also vary widely. In the plant shown in Fig. 10, the whole distillate is obtained in one mass. Some manufacturers collect the distillate in several fractions, whereby the subsequent separation into solid and liquid material is somewhat simplified. The portions distilling over towards the end of the 'run' are so dark-coloured and contaminated with organic impurities that they must be redistilled; hence they are termed 'still-returns.' For the ex-

emplification of the distillation of such 'still-returns,' see Lewkowitsch, 6 Ed. iii. 242.

The best practice is to stop the distillation when dark-coloured distillates make their appearance and to transfer the still residue to a second still, where the residues from several 'runs' are allowed to accumulate. These are then distilled separately, preferably *in vacuo*, and the distillation is carried so far that only pitch remains in the still.

The acid saponification process leads to a greater yield of solid material than does the autoclave process. Whereas the candle material obtained by the latter process may reach 52 p.c., the yield of 'stearine' by 'sulphuric acid saponification' is from 61 to 63 p.c.; hence only 30–32 p.c. of oleic acid results as a by-product in this process, as against 47 p.c. from the autoclave process.

The conversion of oleic acid into candle material is of great practical importance and has formed one of the chief technical problems of the fat industry during the last 80 years. For a full description of the processes employed on a large scale the reader must be referred to Lewkowitsch, Chem. Tech., 6 Ed. iii. 243.

The glycerin in the acid saponification process is obtained in smaller yield and, as has been

shown under GLYCERIN, the quality is not as good as that obtained in the autoclave processes. Hence a combination of these two processes suggests itself, for as regards increase of candle material, the action of sulphuric acid on olein is apparently the same as on oleic acid. The combined method is known as the 'mixed process.'

MIXED PROCESS.

This process consists in hydrolysing the fatty material in an autoclave by means of bases, thus recovering the full amount of glycerin, and then treating the fatty material with concentrated sulphuric acid in the manner described above. Any neutral fat which has escaped hydrolysis in the autoclave is thus saponified. Therefore, in the subsequent distillation of the acidified material, less neutral fat can accumulate in the still than is the case when 'autoclaved,' non-acidified, fatty acids are distilled. Hence the amount of hydrocarbons in the distillates is also reduced.

The yield obtainable from neutral fats by the 'mixed process' is: candle material 61-63 p.c., oleic acid 32-33 p.c., crude glycerin, sp.gr. 1.240, 10 p.c., pitch and loss 2-3 p.c.

The product obtained by the Twitchell process, No. 5b, is too dark to be made into candle material by pressing, such as is feasible with 'autoclaved' material. It is therefore imperative to distil the acids; it is advisable to treat the fatty material, previous to distillation, with concentrated sulphuric acid, as described above, so as to increase the yield of candle material.

The Twitchell process lends itself most advantageously to raw material of low quality and rich in fatty acids, such as 'greases,' which cannot be worked up economically by autoclaving. The yield from the Twitchell process is the same as that from the autoclave or from the mixed process, according to the manner in which the saponified material is treated, except in the case of coconut and palm-kernel oils, where a notable amount of volatile acids is carried away with the steam during the prolonged time of steaming with the reagent.

"STEARINE"-CANDLE MATERIAL.

The solid material obtained by the above processes is known in commerce as 'stearine,' and is chiefly employed in the manufacture of candles (see CANDLES). According to the process by which the stearine is obtained, we differentiate in commerce between 'saponification stearine' and 'distillation stearine.' The 'saponification stearine' originates from those autoclave processes which are not followed by distillation of the fatty acids. The 'distillation stearine' is obtained by all those processes in which distillation is employed in the last instance for the refining of the material.

The 'saponification stearine' consists practically of a mixture of stearic and palmitic acids.

The valuation of this material is based on its melting and solidifying points. The higher these are, the more valuable is the material. A definite iodine value indicates the amount of oleic acid left in the press cakes; a definite difference between the neutralisation and the

saponification values corresponds to neutral fat that has escaped hydrolysis, and has not been pressed out with the oleic acid.

For commercial purposes it is but rarely required to ascertain the proportion of palmitic and stearic acids. If the direct determination of the stearic acid be too troublesome, the candle material may be valued on the basis of its solidifying point and of the neutralisation value.

'Distillation stearine' is also valued on the basis of its melting and solidifying points. These are usually lower than those of the 'saponification stearine.' The iodine value of a 'distillation stearine' furnishes a measure of the amount of 'iso-oleic acid' present; and the difference between the neutralisation and saponification values is a measure of the amount of lactone present. If the amount of hydroxystearic acid be required, the acetyl value must be determined. A complete analysis of 'distillation stearine' embraces the determination of the iodine value, of the neutralisation and saponification values, of the acetyl value, and the direct estimation of stearic acid; palmitic acid is then found by difference.

By means of the iodine value it is possible to differentiate 'saponification stearine' from 'distillation stearine.' The iodine value of the former rarely exceeds a few units, whereas 'distillation stearine' gives iodine values varying, as a rule, between 15 and 30.

The amount of unsaponifiable matter in both kinds of stearine should be negligible. The amount of the ash should be practically *nil*. It is important to determine the ash, as a minute amount, even 0.01 p.c., may lead to guttering of the candle prepared from such material.

J. L.

SAPONINS *v.* GLUCOSIDES and SENEGA. For the evaluation of saponins as frothing agents, see L. Kofler (Chem. Zeit. 1924, 48, 165; Analyst, 1924, 43, 239).

SAPORUBRIN *v.* GLUCOSIDES.

SAPPHIRE *v.* ALUMINIUM; also CORUNDUM.

SARCINE *v.* HYPOXANTHINE.

SARCOLACTIC ACID *v.* LACTIC ACID. For mode of preparation from intercostal proteinous tissue, see Missenden, Chem. News, 1923, 126, 251.

SARD *v.* AGATE; ONYX; QUARTZ.

SARDINE OIL. Highly unsaturated acids are contained in and may be isolated from Japanese sardine oil by the polybromide method and the lithium salt acetone method, and may be converted into methyl esters. By repeated fractional distillation of the esters under reduced pressure, M. Tsujimoto (Kôgyô-Kwagaku Zasshi J. Chem. Ind. Japan) succeeded in isolating *clupanodonic acid* in a nearly pure state. It is a light yellow liquid with a fishy odour; sp.gr. 0.9385 at 15°/4°C., 0.9356 at 20°/4°C., $n_D^{15}=1.5039$, $n_D^{20}=1.5020$; it does not solidify at -50°C., but becomes a semi-solid similar to vaseline at -78°C. The methyl ester is a light yellow liquid, b.p. about 222°C. at 5 mm. The formula of clupanodonic acid is $C_{22}H_{34}O_2$. Among the other highly unsaturated acids of the oil, the acids $C_{18}H_{28}O_2$ and $C_{20}H_{32}O_2$ (and $C_{20}H_{30}O_2$?) are probably present, but in much smaller quantity than clupanodonic acid, and they have not yet been isolated (J. Soc. Chem. Ind. 1923, 42, 1185 A.).

SARDONYX *v.* AGATE and ONYX.

SAROTHAMNINE $C_{15}H_{24}N_2$, an unsaturated alkaloid occurring with sparteine in the common broom, forming crystalline compounds with chloroform, ethyl alcohol, and other solvents (Valeur, Compt. rend. 1918, 167, 26). Possibly identical with the *spartyrine* of Willstätter and Marx, Ber. 1905, 38, 1727. See SPARTEINE.

SARPOKARBOL. Trade name for a preparation of crude carbolic acid. Used as a disinfectant.

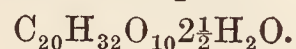
SARPOL, SOLATOL, SOLVEAL. Trade names for preparations of crude carbolic acid. Used as disinfectants.

SARSAPARILLA. (*Sarsaparilla*, U.S. P.; *Sarsæ Radix*, B. P. 1898; *Racine de Salsepareille*, Fr.; *Sarsaparillwurzel*, Ger.) Of the various kinds of sarsaparilla imported into this country that variety which originally came by way of Jamaica, and is still known as 'Jamaica sarsaparilla,' was alone recognised by the British Pharmacopœia until it was deleted in the 1914 revision. The U.S. P. admits Mexican sarsaparilla (from *S. medica* Chamisso and Schlechtendal) and Honduras sarsaparilla (probably from *S. officinalis*, Kunth) in addition to the Jamaica variety. The latter was formerly believed to be the root of *Smilax officinalis* (Kunth; Benth. a. Trim. 289), but observations on a flowering specimen at Kew indicate that the official drug was derived from a distinct species to which Sir J. Hooker gave the name *S. ornata* (Lem.) (Pharm. J. [iii.] 19, 989). It is a woody climbing plant which inhabits Central America, especially the mountains known as the Cordillera of Chiriqui in the isthmus of Panama adjoining Costa Rica, and perhaps other districts in the northern parts of South America. For botanical and other characters, see Pereira (Mat. Med. 3rd ed. 1153) and Flück. a. Hanb. 703. Sarsaparilla is an alterative medicine, employed especially in the treatment of some forms of syphilis, but it is not regarded with the same favour that it was formerly.

Of the constituents of sarsaparilla, with the exception of *starch*, which occurs to the greatest extent in some of the non-official varieties of the drug, the only ones to be described are a trace of *volatile oil* and the crystalline compound *parillin*, identical with *pariglin*, *sarsaparillin*, *parillinic acid* and *smilacin* (e.g. Poggiale, J. Pharm. Chim. 18, 734; 20, 162, 553, 679).

Parillin is deposited in a crystalline form, when an alcoholic extract of the root, after treatment with animal charcoal, is concentrated. When recrystallised from alcohol, it assumes the form of colourless needles. Flückiger (Arch. Pharm. 1877, 210, 532; Pharm. J. [iii.] 8, 488) precipitates the crude parillin from the concentrated alcoholic solution by the addition of water, and then purifies it in the manner described. The yield was about 0.19 p.c. of the root employed. $C_{40}H_{70}O_{18} \cdot 2H_2O$ (Flückiger), $C_{26}H_{44}O_{10} \cdot 2\frac{1}{2}H_2O$ (von Schulz, Arb. aus dem pharmak. Instit. Dorpat, 1896, 14, 14; Diss. Dorpat, 1892), m.p. 177° (von Schulz). It is almost insoluble in cold, though somewhat soluble in hot water; is soluble in alcohol and less so in chloroform. Dilute (10 p.c.) sulphuric acid when heated with parillin gives a green colour, which on further concentration changes to red and brown. It is a glucoside, yielding by

the action of dilute acids *sugar* and *parigenin*. The latter compound was obtained by Flückiger in scaly crystals from its solution in alcohol. It is distinguished from parillin by being quite insoluble even in hot water. Parillin and parigenin seem nearly related to saponin and sapogenin, if not also to cyclamin and cyclamiretin; but parillin is not acrid and its powder does not cause sneezing. The mother-liquor of smilacin contains, according to von Schulz, *sarsasaponin*, crystals, $C_{22}H_{36}O_{10} \cdot 2H_2O$, and *sarsaparilla saponin*, amorphous,



For the saponins of the sarsaparilla root, see Kaufmann and Fuchs (Ber. 1923, 56, [B.] 2527). According to J. Murayama and T. Itagaki (Yakugakuzasshi J. Pharm. Soc. Japan, 1923, No. 501, 783) about 5 p.c. of a saponin was isolated as a white amorphous powder from an alcoholic extract of crushed *Panax repens*, Maxim. It melts at 180° – 190° , and has acidic properties, which furnishes an example for the hypothesis of Asahina and Momotani (*ibid.* 1914, No. 384, 117). It gives a red coloration with concentrated sulphuric acid in acetic anhydride. On hydrolysis with 3 p.c. hydrochloric acid, it yields dextrose and a sapogenin (15 p.c.), white lustrous needles, m.p. 303° – 304° . The sapogenin gives the same colour reactions as the saponin, but has no bitter taste. It gives two diacetyl derivatives, one, plates, melting at 207° – 210° , and the other, needles, melting at 257° – 260° (J. Soc. Chem. Ind. 1924, 43, B. 276). G. B.

SARSAPARILLIN *v.* SARSAPARILLA.

SARTON. A trade name of a preparation from the fruits or seeds of *Glycine Soja* (Sieb. and Zucc.), [*Soja hispida* (Mönch)], cultivated in China and Japan. Used in the treatment of diabetes.

SASSAFRAS OIL *v.* OILS, ESSENTIAL.

SASSOLITE (*Sassolin* of D. L. G. Karsten, 1800). The mineralogical name for boric acid, H_3BO_3 , crystallised in the triclinic system. The crystals have a highly perfect cleavage, with pearly lustre, in one direction. They are very soft (H.=1) and greasy to the touch; sp.gr. 1.48. Although of abundant occurrence in solution in the Tuscan lagoons, it is not often met with in the solid state, but it was so observed by P. Mascagni around the 'soffioni' at Sasso in Tuscany. In the crater of Vulcano, one of the Lipari Islands, it occurs, however, in some abundance as a layer on native sulphur, forming loose, friable aggregates of small, pearly white scales, the masses being often tinged yellow by admixed sulphur. Here it was formerly collected commercially. It is also deposited as a sublimation around the fumaroles of Vesuvius.

L. J. S.

SATIN-SPAR and **SATINITE** *v.* GYPSUM.

SATIN WHITE. A gelatinous aluminium hydroxide mixed with calcium sulphate and free lime, made by precipitating aluminium sulphate with excess of lime in fairly strong solution. Used in coating paper.

SATIVIC ACID. Tetrahydroxystearic acid $CH_3 \cdot (CH_2)_4 [CH(OH)]_2 CH_2 \cdot [CH(OH)]_2 \cdot (CH_2)_7 \cdot CO_2H$ (Eckert, Chem. Soc. Abst. 1917, i. 317). Prepared by the oxidation of linoleic acid (Reinger, Ber. deut. Pharm. Ges. 1922, 32, 124).

SAUROL. An oil obtained by distilling a bituminous shale found in a mine near Lake Lugano, Switzerland. The purified oil contains 6-7 p.c. of sulphur in organic combination, and closely resembles ichthyol in its therapeutic properties (Méran, Pharm. J. 1917, 98, 43).

SAVIN, OIL OF, v. OILS, ESSENTIAL, and SABINOL.

SAXIFRAGIN v. Barium nitrate, art. BARIUM.

SAXON BLUE. A term occasionally applied to a solution of indigo in sulphuric acid. Used also as a synonym for smalt.

SAXON GREEN. Emerald green v. PIGMENTS.

SAXONITE v. PERIDOTITE.

SCAMMONY v. GUM RESINS.

SCANDIUM. Sym. Sc. At.wt. 45.1. The discovery of *scandia* by Nilson in 1879 was an event of the greatest scientific interest, inasmuch as this oxide and its compounds have properties corresponding with those of the hypothetical element '*ekaboron*,' the existence of which had been predicted by Mendeléeff to fill a gap in the periodic classification of the elements. The element, *scandium*, is distinguished from the allied metals of the cerium and yttrium groups by its low atomic weight and by the feeble basic strength of its oxide (Nilson, Ber. 1879, 551, 554; 1880, 1430, 1439; Compt. rend. 1879, 88, 645; 1880, 91, 56, 118; Cleve, *ibid.* 1879, 89, 419; Mendeléeff, Ber. 1881, 14, 2821). According to Aston, scandium is simple with an atomic weight of 45.

Occurrence.—In varying quantities in the following rare minerals: thortveitite from Saetersdalen, Norway, contains 42 p.c. Sc_2O_3 (*q.v.*), ytterbite (gadolinite), yttrotitanate, wiikite (Impilako, Finland, 1 p.c. Sc_2O_3), orthite (Impilako), auerlite, cerite, keilhauite, mosandrite, orangite, pyrochlore, äschynite, monazite, thorite, thorianite. Scandium is almost constantly associated with tin ores and is found in many specimens of wolframite. It is also frequently associated with zirconium; Brazilian zirconia contains notable quantities of scandium fluoride (Crookes, Proc. Roy. Soc. 1908, 80, A. 516; R. J. Meyer, Sitzungsber. Akad. Wiss. Berlin, 1910, 398; 1911, 379; G. Eberhard, *ibid.* 1908, 851; 1910, 404; Zeitsch. anorg. Chem. 1908, 60, 134; C. James, J. Amer. Chem. Soc. 1918, 40, 1674).

P. and G. Urbain (Compt. rend. 1922, 174, 1310, 1442) have described the following process for the extraction of scandium from thorveitite. The mineral is fused with sodium hydroxide and the residue left after extracting the fused mass with water is dissolved in the smallest possible quantity of sulphuric acid. From this solution the rare earths are precipitated as fluorides by the addition of an excess of hydrofluoric acid. The fluorides are decomposed by sulphuric acid and scandium bisulphate crystallises out on concentrating the solution. The sulphates are converted into nitrates by way of the hydroxides, and the solution of nitrates is concentrated on a water-bath until it is free from excess. To the concentrated solution an excess of powdered potassium sulphate is added until the solution is saturated. After three days the double scandium potassium sulphate is filtered off and washed with a saturated solution of potassium

sulphate. Any scandium remaining in the mother-liquors is reprecipitated as hydroxide and passed through the same process. The double sulphate may be dissolved in aqueous ammonium carbonate, and from the solution, on warming, scandium hydroxycarbonate is precipitated. The residue of the scandium in the mother-liquors may be recovered by conversion into its acetylacetone, which is soluble in chloroform and sublimes when heated *in vacuo* at 200°.

Separation and Purification.

1. *Fractional decomposition of the nitrates.*—Aqueous solutions of the nitrates are evaporated until the normal nitrates crystallise; these salts are then decomposed by gradually raising the temperature when nitrous fumes are evolved and a vitreous mass of basic nitrates is produced. This product dissolves readily in hot water, and the cooled solution deposits the basic nitrates of the less electropositive rare earth metals. The operation is repeated systematically until scandium, neoytterbium, and lutecium are concentrated in the most readily decomposable fractions. Scandium nitrate is completely decomposed at temperatures at which neoytterbium and lutecium nitrates yield only basic nitrates (Nilson, *v. supra*; Marignac, Compt. rend. 1878, 87, 578).

Meyer and Goldenberg find that iodic acid may be used as potassium iodate to separate thorium from scandium in a nitric acid solution, the thorium iodate being precipitated as a flocculent amorphous precipitate (Chem. News, 1912, 106, 13). Another method is to drop slowly the neutral solution of scandium containing thorium into a concentrated solution of ammonium tartrate which is kept well stirred, and the clear solution is precipitated with ammonia while boiling. The scandium separates as scandium ammonium tartrate.

2. *The basic salt method of separation.*—The somewhat troublesome decomposition of the nitrates by heat is obviated by using Auer v. Welsbach's method of treating the oxides with insufficient nitric acid to convert all the bases into normal nitrates. The pasty mass is digested with alcohol when the normal nitrates dissolve leaving behind the basic nitrates. The decomposed fractions contain scandium, lutecium, and neoytterbium, the less decomposed fractions consist mainly of the basic salts of yttrium and the terbium group whilst the cerium metals remain as soluble normal nitrates and are thus completely eliminated. Erbium is separated from lutecium, neoytterbium, and scandium by adding water to the hot solution of the basic salts until a permanent turbidity is obtained, and digesting until the last-mentioned metals are precipitated, leaving erbium in solution (Monatsh. 1883, 4, 630; 1884, 5, 508; Schottländer, Ber. 1892, 25, 378).

Drossbach adapts the basic salt method to the chlorides instead of the nitrates (Ber. 1902, 35, 2826).

3. *Miscellaneous methods.*—Scandium is separated from neoytterbium and lutecium by taking advantage of the circumstance that although in its slight electro-positive character the metal is allied to these elements of the yttrium group, yet it differs from them, and

resembles the more electro-positive cerium metals in forming a double potassium sulphate only very sparingly soluble in aqueous potassium sulphate (Nilson, *v. supra*).

Hydrochloric acid solutions of scandium when treated with solid sodium silicofluoride and boiled for 30 mins. give a precipitate containing this element free from the other rare earth metals. A separation from all these elements excepting thorium is effected by boiling a neutral solution with sodium thiosulphate when scandium thiosulphate is precipitated. Fractional sublimation of the anhydrous chlorides leads to a separation, scandium chloride being less volatile than the thorium salt. Boiling with excess of sodium carbonate brings thorium into solution, whilst the sparingly soluble scandium sodium carbonate $4\text{Na}_2\text{CO}_3 \cdot \text{Sc}_2(\text{CO}_3)_3 \cdot 6\text{H}_2\text{O}$ is deposited (R. J. Meyer, *Zeitsch. anorg. Chem.* 1908, 60, 134; 1910, 67, 398).

For a method of separating scandium oxide from the residual oxides after wolframite has been used for the preparation of sodium tungstate, see Sterba-Böhm, *Zeitsch. Elektrochem.* 1914, 20, 289; Lukens, *J. Amer. Chem. Soc.* 1913, 35, 1470.

Scandium hydroxide $\text{Sc}(\text{OH})_3$ is precipitated by ammonia as a white gelatinous mass.

Scandium oxide (*scandia*) Sc_2O_3 , white powder, sp.gr. 3.864, sparingly soluble in cold, easily soluble in hot, acids. The scandium salts with colourless acid radicals are themselves devoid of colour.

Scandium sulphide Sc_2S_3 is a light yellow powder obtained by heating the sulphate in hydrogen sulphide.

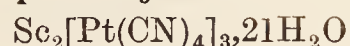
Scandium sulphate $\text{Sc}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$ is the most soluble of the sulphates of the rare earths, 100 c.c. of water at 25° dissolving 54.6 grms. Above 100° it is converted into the dihydrate; the double sulphate $\text{Sc}_2(\text{SO}_4)_3 \cdot 3\text{K}_2\text{SO}_4$ is only slightly soluble in saturated solutions of alkali sulphates. **Scandium selenate** $\text{Sc}_2(\text{SeO}_4)_3 \cdot 8\text{H}_2\text{O}$ forms rhombic prisms.

Scandium nitrate $\text{Sc}(\text{NO}_3)_3 \cdot 4\text{H}_2\text{O}$ separates only from highly concentrated solutions, and when heated yields two basic nitrates.

Scandium fluoride ScF_3 forms three ammonium scandifluorides, $(\text{NH}_4)_3\text{ScF}_6$, which by treatment with water give $(\text{NH}_4)_2\text{ScF}_5$ and $(\text{NH}_4)\text{ScF}_4$, (Sterba-Böhm, *Bull. Soc. chim.* 1920, [iv.] 27, 185). For sodium scandium fluoride and sulphate, see Meyer, Wassjuchnov, Drapier and Bodländer (*Zeitsch. anorg. Chem.* 1914, 86, 257; *Chem. Soc. Abstr.* 1914, ii. 369).

Scandium chloride ScCl_3 and **bromide** ScBr_3 each crystallise with $6\text{H}_2\text{O}$: the **aurichloride** $3\text{ScCl}_3 \cdot 2\text{AuCl}_3 \cdot 21\text{H}_2\text{O}$ yellow needles, is very deliquescent. Scandium chloride melted under pressure in a quartz apparatus, in order to avoid loss by sublimation, melts at 939° . The specific conductivity is 0.51 at 959° , 0.55 at 969° , 0.57 at 981° , and 0.59 at 991° . A marked decrease in conductivity is observed as the molten salt solidifies on cooling. The observed results resemble those of thorium chloride rather than those of aluminium chloride, the conductivity of the last-named being from 10^{-5} to 10^{-6} times as much (W. Biltz and W. Klemm, *Zeitsch. anorg. Chem.* 1923, 131, 22; *Chem. Soc. Abstr.* 1924, 126, ii. 184).

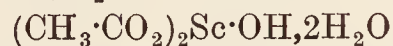
Scandium platinoeyanide



monoclinic prisms, crimson by transmitted, green by reflected, light, dissolving to a colourless solution. On heating the red crystals become yellow owing to the loss of three mols. of water.

Scandium borate ScBO_3 , white powder, soluble in dilute acid, produced by fusing together scandia and boric acid.

Scandium salts of the fatty acids are more soluble in cold than in hot water; the **formate** $(\text{HCO}_2)_2\text{Sc} \cdot \text{OH} \cdot \text{H}_2\text{O}$ and **acetate**



are crystalline; the salts of the homologous acids are amorphous (Crookes, *Phil. Trans.* 1908, 209, A, 15; 1910, 210, A, 359). These memoirs contain descriptions of many other scandium salts. See also Meyer (*Zeitsch. anorg. Chem.* 1914, 86, 257).

Scandium oxalate $\text{Sc}_2(\text{C}_2\text{O}_4)_3 \cdot 5\text{H}_2\text{O}$, crystalline powder, soluble in ammonium oxalate, forming double oxalates, and dissolving less readily in dilute sulphuric acid than the oxalates of other rare earth metals (Cleve, *Compt. rend.* 1879, 89, 419; Brauner, *Chem. Soc. Trans.* 1898, 73, 951).

Scandium acetylacetone (Morgan and Moss, *Chem. Soc. Trans.* 1914, 105, 196).

Spectra.—Spark spectrum (Thalén, *Compt. rend.* 1880, 91, 45; Nilson, *v. supra*; Exner and Haschek, *Ber. Wien. Akad.* 1900, 109, IIa, 122).

Arc spectrum (Exner and Haschek, *Die Wellenlängen der Bogenspektren*, 1904; Crookes, *Proc. Roy. Soc.* 1919, A, 95, 438).

Arc spectrum in relation to solar spectrum (*v.* Lockyer and Baxandall, *Proc. Roy. Soc.* 1905, 538; Fowler, *Phil. Trans.* 1908, 209, A, 47).

Electric furnace spectrum (King, *Astrophys. J.* 1921, 54, 28). G. T. M.

SCAPOLITE. A group of rock-forming minerals analogous in composition to the plagioclase-feldspars with the addition of radicles NaCl , CaSO_4 , &c., as in the sodalite group. The several hypothetical molecules suggested to explain the variations in composition are:

Chloride-marialite	$\text{NaCl} \cdot 3\text{NaAlSi}_3\text{O}_8$ (sp.gr. 2.56)
Sulphate-marialite	$\text{Na}_2\text{SO}_4 \cdot 3\text{NaAlSi}_3\text{O}_8$
Carbonate-marialite	$\text{Na}_2\text{CO}_3 \cdot 3\text{NaAlSi}_3\text{O}_8$
Sulphate-meionite	$\text{CaSO}_4 \cdot 3\text{CaAl}_2\text{Si}_2\text{O}_8$
Carbonate-meionite	$\text{CaCO}_3 \cdot 3\text{CaAl}_2\text{Si}_2\text{O}_8$ (sp.gr. 2.77)

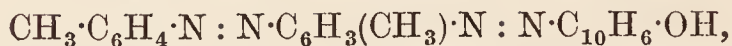
Crystals are tetragonal. Meionite from the ejected limestones blocks of Vesuvius forms small glassy crystals; whilst common scapolite, intermediate in composition between meionite and marialite, is often found as large dull crystals, *e.g.* in Finland, south Norway, Ontario, New York. The mineral occurs in metamorphic rocks, particularly crystalline limestones. Clear pink scapolite suitable for use as a gem-stone ($\text{H} = 6$) has been found at the ruby mines near Mogok, in Upper Burma; and clear yellow material has been found in Madagascar.

L. J. S.

SCAPTIN *v.* DIGITALIS.

SCARLET, ATLAS, BIEBRICH, BRILLIANT, COCHINEAL, CROCEÏN, DOUBLE, *v.* AZO-COLOURING MATTERS.

SCARLET OCHRE. *Venetian red v.* PIGMENTS.

SCARLET RED (medicinal), *Fettponceau R.*

prepared from diazotised *o*-aminoazotoluene and β -naphthol, is a dark reddish-brown powder, m.p. about 185°. It is insoluble in water, sparingly so in cold alcohol, acetone, or benzene. One part dissolves in 15 of chloroform, and it is readily soluble in fats and fatty oils, and to a less extent in vaseline and paraffin. Pure scarlet red is used for stains in microscopical work, and has been shown to have valuable therapeutic properties (Fischer, *Münch. Medizin. Wochensch.* 1906, No. 42; *Semaine médicale*, 1908, 114).

It is applied in the form of an ointment to wounds, burns, ulcers, mallenders, bruised knees, &c., both in human and veterinary medicine, but it has only given successful results when applied to clean flat wounds of a fresh red colour. Being somewhat irritant, it should not be left in place continuously longer than a day. Its use depends on the power it possesses of forming thick resistant epithelial layers.

The ointment may be prepared by rubbing up 8 grms. of scarlet red with chloroform oil until the chloroform has evaporated, then adding enough yellow vaseline to form 100 grms. of ointment; according to Reinhardt the chloroform may be dispensed with. The ointment may also be prepared by rubbing together 1-2 grms. of scarlet red with equal parts of lanoline and *unguentum paraffine* to make 20 grms. The subcutaneous ingestion of scarlet red has also been investigated by Fischer; see also Werner, *Münch. Medizin. Wochensch.* 1908, 2267.

Scarlet red gives a blue-green solution with sulphuric acid; on addition of water the colour becomes more blue than scarlet. Hydrochloric acid acts similarly, the colours being of a more reddish tinge, whilst nitric acid decomposes the stain. 0.5 gm. dissolved in 2-3 c.c. of boiling glacial acetic acid, and treated with a little zinc-dust, gives a transitory blue-red colour, which finally changes to a pale wine yellow. Drops of this liquid on filter paper become coloured dirty red-blue (Reinhardt, *Apotheker Zeit.* 1909, No. 10). According to a note in the *Pharm. J.* 1912, 452, aminoazotoluene itself when used in the form of an 8 p.c. ointment is equally, if not more, effective than scarlet red. Both substances may be employed with advantage in blue ointment for syphilitic ulcers and as dusting powders in 4-8 p.c. strength with boric acid.

Literature.—Kracja, *Münch. Medizin. Wochensch.* 1908, 1969; Stoeber, *ibid.* 1910, No. 14; Kähler, *Medizin. Klinik.* 1908, 836; Wessley, *ibid.* 1910, No. 14; Bruhn, *Therapeutische Neuheiten*, 1908, No. 9; Gaudier, *Rev. de Therapeutique*, 1910, 671; Lemaire, *Echo Medic. du Nord*, 1910, June 12; Straus, *Deutsche Medizin. Wochensch.* 1910, No. 19; Pein, *Therapie der Gegenwart*, 1910, No. 3; Köster, *Zeitsch. Veterinärkunde*, 1910, No. 7; Picard, *Rev. Gener. de medicine Vétérinaire*, 1910, October 5.

SCARLET RUNNER BEAN, *Phaseolus multiflorus*, Lam. The air-dried roots of this plant, according to Power and Salway, contain (1) an enzyme which readily hydrolyses amygdalin; (2) a small amount of an essential oil; (3) furan- β -monocarboxylic acid $\text{C}_5\text{H}_4\text{O}_3$, m.p.

120°; (4) allantoin; (5) a phytosterol $\text{C}_{27}\text{H}_{44}\text{O}$, m.p. 130°; and apparently a little pentatriacontane $\text{C}_{35}\text{H}_{72}$; (6) a small amount of substance having the characters of a phytosterol glucoside (*Chem. Soc. Trans.* 1913, 103, 399); (7) a crystalline glucoside *phaseosaponin* $\text{C}_{30}\text{H}_{84}\text{O}_{20}$, m.p. 238°, which on hydrolysis yields *phaseosapogenin* $\text{C}_{26}\text{H}_{44}\text{O}_4$ and a sugar which appeared to be rhamnose; (8) a mixture of solid and liquid fatty acids, the latter being unsaturated. The roots also contain in addition to some resin, a quantity of sugar which yielded *d*-phenylglucosazone, m.p. 212°. No alkaloid is present, nor compound capable of yielding hydrogen cyanide. Contrary to the statement of Lindley and Moore (*Treasury of Botany*, edit. 1899, Part II. p. 874) the roots possess no toxic properties.

SCARLET, WOOL, *v.* AZO-COLOURING MATTERS.

SCARLET, XYLIDINE, *v.* AZO-COLOURING MATTERS.

SCATOLEACETIC ACID, **SCATOLECARBOXYLIC ACID** *v.* INDOLES.

SCATOLES *v.* INDOLES.

SCHÄFFER'S ACID. 2-Naphthol-6-sulphonic acid *v.* NAPHTHALENE.

SCHEEL'S GREEN *v.* ARSENIC. According to Bornemann (*Zeitsch. anorg. Chem.* 1922, 124, 36) Scheele's green is not acid copper orthoarsenite CuHAsO_3 , but a neutral arsenite $3\text{CuO}, \text{As}_2\text{O}_3, x\text{H}_2\text{O}$. The composition varies with the method of preparation, being richer in copper oxide the larger the amount of alkali employed.

SCHEELITE. Native calcium tungstate, CaWO_4 , crystallised in the tetragonal system. For a pale-coloured, stony-looking mineral it is surprisingly heavy (sp.gr. 6.0), and it was consequently early known in Sweden as *tung-sten*, meaning 'heavy stone.' This name was transferred to the element discovered in this mineral by K. W. Scheele in 1781, whilst the mineral itself came to be known as scheelerz and later as scheelite. Well-shaped crystals are of frequent occurrence; these have the form of acute square pyramids, with distinct cleavages parallel to their faces. The colour is greyish, yellowish, or brown, and the lustre vitreous to resinous; hardness $4\frac{1}{2}$. Analyses show the presence of up to 8 p.c. of molybdic acid replacing the tungstic acid; and the variety known as cuproscheelite forms a passage to cuprotungstite (CuWO_4). Scheelite is decomposed by hydrochloric acid with the separation of tungstic acid. Crystals of scheelite partly or completely altered to wolframite are found at Trumbull and Monroe in Connecticut, and at Kimpu-san in province Kai, Japan. These pseudomorphs from Japan have been incorrectly described as tetragonal iron tungstate under the name 'reinite.'

Scheelite occurs together with wolframite in veins of tin ore, and with gold in quartz-veins traversing granite and gneiss. As an ore of tungsten (WO_3 80.6; W 63.9 p.c.) it is of much less importance than wolframite (*q.v.*). By the ordinary methods of separation in water any scheelite present in the ore is collected with the wolframite, unless the latter is further separated from tin ore by the electro-magnet. At only a few places is scheelite mined alone, *e.g.* at Hillsgrove in New South Wales, the Otago gold-

field in New Zealand, Parada in north Queensland, King Island off Tasmania, Hartley district in Rhodesia, California, and in Nova Scotia. Its uses are the same as those of wolframite (*q.v.*). L. J. S.

SCHLEICHERA TRIJUGA is a large deciduous tree belonging to the natural order *Sapindaceae*, common in India, Ceylon, and the East Indies, the seeds of which appear to contain a cyanogenetic glucoside. They are the source of the so-called 'Macassar' oil, known also as Kon oil, Kusum oil, &c. According to Sen-Gupta (*J. Soc. Chem. Ind.* 1920, 88 T) the seeds have the following composition:—

Moisture	Oil	Proteins	Carbohydrates	Fibre
3.20	67.13	18.20	6.14	3.40
Ash	Total N	N as true proteins	N as amides, &c.	
1.93	2.912	2.436	0.448	

The hydrocyanic acid yielded by the seeds may amount to 0.574 p.c.

Schleichera fat is a solid, yellowish-white in colour, changing to dark brown on prolonged heating, and of a pleasant smell. Sp.gr. $99^{\circ}/15^{\circ}=0.86$, m.p. 21° – 31° , solidifying point 29° – 18° , saponification value 229.1, iodine value 52.4. Refractive index at 21° 1.46757; acid value 13.06. For other details see Sen-Cupta (*l.c.*).

SCHLIPPE'S SALT. *Sodium sulphantimonate v. ANTIMONY.*

SCHOENITE v. PICROMERITE.

SCHÖLLKOPF'S ACID. 1-Naphthol-8-sulphonic acid or naphthasultone v. NAPHTHALENE.

SCHORL v. TOURMALINE.

SCHORLOMITE v. TITANIUM.

SCHULTZE'S POWDER v. EXPLOSIVES.

SCHWARTZITE v. FAHLORE.

SCHWEINFURTH GREEN. Emerald green v. ARSENIC; also PIGMENTS.

SCHWEITZER'S REAGENT. A solution of hydrated cupric oxide in ammonia, used as a solvent for cellulose (*v. CELLULOSE*).

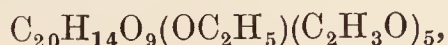
SCILLA, SCILLAIN, SCILLIN, SCILLI-PICRIN, SCILLITIN, SCILLOTOXIN, v. SQUILL.

SCLERERYTHRIN v. ERGOT.

SCOPARIN, the colouring matter of the *Cytisus scoparius* (Link.), has been investigated by Stenhouse (*Annalen*, 78, 15), by Hlaziwetz (*Annalen*, 138, 190), and by Goldschmiedt and v. Hemmelmayer (*Monatsh.* 14, 202).

Scoparin $C_{20}H_{20}O_{10} + 5H_2O ?$ ($C_{22}H_{22}O_{11}$, Herzig and Tiring, *Monatsh. Chem.* 1918, 39, 253), crystallises in small yellow needles, m.p. 202° – 219° , and is soluble in alkaline liquids with a pale-yellow colour. From a hot aqueous solution it is deposited on cooling in a gelatinous condition. The following derivatives have been prepared:

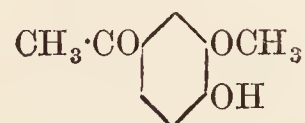
Hexacetylscoparin $C_{20}H_{14}O_{10}(COCH_3)_6$, colourless prisms, m.p. 255° – 256° ; *hexabenzoylscoparin* $C_{20}H_{14}O_{10}(C_7H_5O)_6$, yellow crystalline powder, m.p. 148° – 150° ; *scoparin ethyl ether* $C_{20}H_{19}O_9(OC_2H_5)$, needles, m.p. 272° ; and *acetyl scoparin ethyl ether*



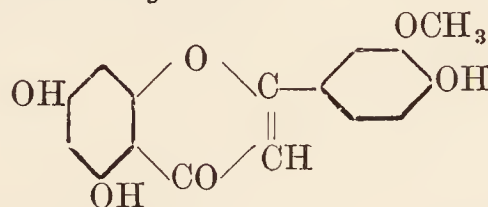
needles, m.p. 140° – 141° (G. and H.).

By fusion with potash scoparin gives *vanillic acid*, *protocatechuic acid*, *acetic acid*, and *phloro-*

glucinol (H.), and by the more gentle action of the alkali *phloroglucinol* and *acetylcatecholmono-methyl ether*



(G. and H.) (*Perkin, Chem. Soc. Proc.* 1899, 15, 123). With boiling hydriodic acid scoparin yields 1 molecule of methyl iodide and a new colouring matter *scoparein* (P.) is formed, which dyes shades almost identical with those given by luteolin. Scoparin itself is but a feeble dyestuff, and its tinctorial properties are almost indistinguishable from those of vitexin (*Vitex littoralis*) [*A. Cunn.*]. According to Perkin (*Chem. Soc. Trans.* 1900, 77, 423) scoparin is probably *methoxyvitexin*, and whereas vitexin is closely related to apigenin, vitexin is derived from *luteolin methyl ether*



See also BROOM TOPS.

A. G. P.

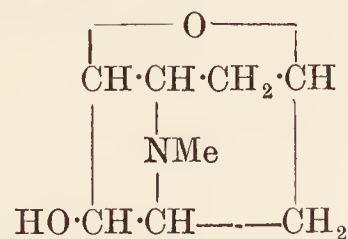
SCOPOLAMINE v. HYOSCINE. Much confusion and controversy have arisen as to the relationship between, and the identity of, the alkaloids hyoscine, scopolamine, and atropine; but there is good reason to believe the names have been variously applied to the *lævo*-rotatory and racemic forms of the same base, though recent work has shown that eight optical isomers are possible.

In England and the United States the term hyoscine is used in the respective pharmacopœias to designate the *lævo*-base, it is therefore adopted in this dictionary, and the name *i*-scopolamine, which has elsewhere been retained for the inactive base, is replaced by *d*-*l*-hyoscine. A more general adoption of the name atropine for the latter would draw a parallel between hyoscyamine-atropine and hyoscine-atropine, and should the inactive alkaloid find wider application in medicine a reversion to the use of a distinctive name will prove desirable to prevent confusion.

Hyoscine v. TROPEINES.

For scopolamine poisoning and the detection of scopolamine in the tissues, *v. Brüning, Ber. Deuts. Pharm. Ges.* 1923, 33, 103. F. H. C.

SCOPOLINE (*Oscine*) $C_8H_{13}O_2N$ or



is a vegetable alkaloid said to occur in crude belladonna (Merling, *Ber.* 1884, 17, 384). It is formed by boiling hydrochloric acid or baryta water with scopolamine (hyoscine) or scopolamine hydrobromide, when it yields tropic acid in addition to scopoline (Ladenburg and Roth, *ibid.* 1884, 17, 151; Luboldt, *Chem. Zentr.* 1895, ii. 896; *Arch. Pharm.* 1898, 236, 11; Pinner, *Chem. Zentr.* 1898, i. 679; see also Hesse, *Annalen*, 1891, 261, 100; *ibid.* 1892, 271, 114).

Scopoline is a tertiary inactive base, containing one methyl group attached to nitrogen, and is closely allied to tropine, from which it differs by the substitution of one oxygen atom for two hydrogen atoms. It has been found that the base combines with hydrogen bromide to yield *bromohydroscopoline* $C_8H_{12}NBr(OH)_2$ which with reducing agents yields *hydroscopoline* $C_8H_{13}N(OH)_2$ (Schmidt, Chem. Zentr. 1905, i. 970; Arch. Pharm. 1909, 247; Ladenburg, Annalen, 1893, 276, 345; Hesse, *ibid.* 84; J. pr. Chem. 1902, [ii.] 66, 194; Hess and Suchier, Ber. 1915, 48, 2057; Schmidt, Ber. 1916, 49, 164; 1918, 51, 1281; King, Chem. Soc. Trans. 1919, 481; Hess, Ber. 1916, 49, 2337, 2745; 1918, 51, 1007; 1919, 52, B, 1947; Hess and Wahl, Ber. 1922, 55, 1979).

It forms colourless, prismatic, very hygroscopic crystals, m.p. 109° , subliming at 90° , b.p. 241° – 243° . Scopoline is readily reduced to *hydroscopoline* which contains two hydroxyl groups, and which, when oxidised with chromic acid, yields *methylpiperidine dicarboxylic acid* $C_8H_{13}O_4N \cdot H_2O$, m.p. 214° – 216° . Oxidised with chromic acid, scopoline yields pyridine methochloride, whilst when oxidised with barium permanganate it forms *scopoligenine* $C_7H_{11}NO_2$, m.p. 205° – 206° , a secondary base which, when treated with methyl iodide, is reconverted into scopoline. Scopoligenine forms a nitroso derivative $C_7H_{10}O_2N \cdot NO$, m.p. 174° – 175° (Luboldt, l.c. 22; Schmidt, Arch. Pharm. 1894, 232, 409; 1905, 243, 559; Chem. Zentr. 1896, i. 1199).

Scopoline readily forms esters (Luboldt, l.c. 33).

Methylscopoline forms a light yellow thick fluid, b.p. 244° (decomp.), readily soluble in water, alcohol, or ether.

Acetyl-scopoline $C_8H_{12}O_2N(COMe)$ is obtained by heating scopoline with acetic anhydride or chloride at 100° – 130° (D. R. P. 79864). It has m.p. 53° , b.p. above 250° . Is readily soluble in organic solvents.

Benzoyl-scopoline is obtained by the action of benzoic anhydride on scopoline, by the repeated evaporation of scopoline benzoate with dilute hydrochloric acid, or by the action of a current of the latter gas on an ethereal solution of scopoline and benzoic acid (D. R. P. 79864; Hesse, Annalen, 271, 119). It forms a crystalline mass, m.p. 68° – 70° . *Cinnamoyl-scopoline* is formed similarly. *Salicyl-scopoline* forms needles insoluble in water, m.p. 105° .

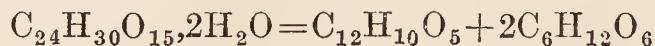
A number of compounds of scopoline and its derivatives with the halogen and other acids, and also with platini- and auri-chlorides, are known (Schmidt, Chem. Zentr. 1902, ii. 844; Arch. Pharm. 1917, 255, 72; Gadamer and Hammer, *ibid.* 1921, 259, 110; D. R. P. 228204; and also nearly all the above references).

Tropyl derivatives of scopoline have been prepared by Luboldt (Arch. Pharm. 236, 40).

For the physiological action of scopoline and its derivatives, see Schiller (Chem. Zentr. 1896, ii. 1039).

The name **scopolin** was given by Eykman to a glucoside of scopoletin which he isolated from the root of the *Scopolia japonica* (Maxim) (Rec. trav. chim. 3, 169; Pharm. J. 1884, 15, 81; Ber. 1892, 3078). This substance has the composition $C_{24}H_{30}O_{15} \cdot 2H_2O$, forms needles,

m.p. 218° , soluble in cold water and in alcohol, but not in chloroform or ether. Its solution in sulphuric acid has a blue fluorescence and decomposes on boiling thus:



v. HORSE CHESTNUT.

SCORODITE. Hydrated ferric arsenate $FeAsO_4 \cdot 2H_2O$, crystallised in the orthorhombic system. Brilliant crystals often of a characteristic sage-green colour are known from Cornwall, Saxony, Brazil, &c. Sp.gr. 3.1–3.2. More often it is earthy or compact (iron-sinter or jogynaite). The mineral is of common occurrence as an alteration product of mispickel ($FeAsS$) in the upper oxidised portion of mineral veins; and is sometimes associated with free gold and cassiterite.

L. J. S.

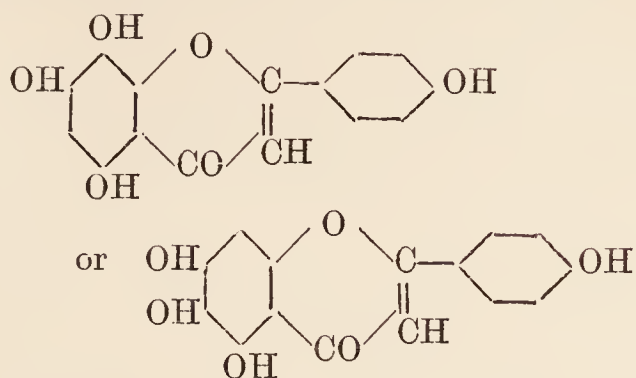
SCOVILLITE v. RHABDOPHANE.

SCUTELLARIA ALTISSIMA. *Scutellarin*. If the flowers and leaves of *Scutellaria altissima* are extracted with water the solution on keeping deposits crystals of *scutellarin* $C_{21}H_{18}O_{12}$ (Molisch and Goldschmiedt, Monatsh. 1901, 22, 68; Goldschmiedt and Zerner, *ibid.* 1910, 31, 439). It melts above 310° , is sparingly soluble in the usual solvents, and the alcoholic solution gives with lead acetate a red precipitate, and with ferric chloride a green coloration passing into red on heating. With the haloid acids and sulphuric acid in the presence of acetic acid orange-red crystalline oxonium compounds separate, which are readily decomposed in contact with water. *Penta-acetyl-scutellarin* $C_{21}H_{13}O_{12}(C_2H_3O)_5$ is colourless, melts at 263° – 265° , and from this by gentle hydrolysis scutellarin can be regenerated. On fusion with alkali *p-hydroxybenzoic acid* and a second substance crystallising in leaflets are produced. When concentrated sulphuric acid is added to scutellarin suspended in water until a clear liquid is obtained, on dilution *scutellarein* $C_{15}H_{10}O_6$ is precipitated and *glycuronic acid* is present in the solution. The hydrolysis of scutellarin cannot be effected by means of dilute acids, though this takes place, however, when its suspension in glacial acetic acid is treated with sulphuric acid, the oxonium sulphate thus obtained being evidently that of scutellarein.

Scutellarein when pure forms yellow crystals melting above 300° and is soluble in alkaline solutions with a yellow colour. Lead acetate solution gives a reddish-yellow precipitate and ferric chloride a reddish-brown coloration. On acetylation scutellarein gives the colourless *tetra-acetyl* compound $C_{15}H_6O_6(OAc)_4$, m.p. 235° – 237° , whereas with ethereal diazomethane *scutellarein trimethyl ether* $C_{15}H_7O_3(OMe)_3$, m.p. 189° – 190° , is formed. By means of methyl alcoholic potash and methyl iodide the *tetra-methyl* compound $C_{15}H_6O_2(OMe)_4$ can be obtained in small amount. By fusion with potassium hydrate *p-hydroxybenzoic acid* and *phloroglucinol* (?) are produced, whereas a boiling 12 p.c. solution of the alkali gives *p-hydroxyacetophenone* and a substance which gives the pine-wood reaction of phloroglucinol. Dilute nitric acid gives picric, oxalic, and 3.5-dinitro-4-hydroxybenzoic acids.

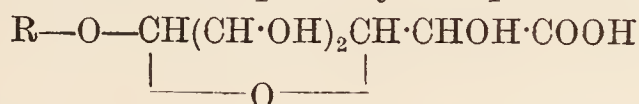
Scutellarein, according to Goldschmiedt and

Zerner, is a 1:3:4:4' or 1:2:3:4' tetra-hydroxyflavone.



According to Bargellini (Gazz. chim. ital. 1919, 49, ii. 47; Chem. Soc. Abstr. 1919, i. 545) the latter view is correct.

Scutellarein can probably be represented as



R in this formula representing the scutellarein nucleus.

A. G. P.

SCYTHE-STONE v. WHETSTONE.

SEALING-WAX. (*Cire à cacheter*, Fr.; *Siegel-lack*, Ger.) The Hindoos from time immemorial have possessed the resin lac, and were long accustomed to use it for sealing manuscripts before it was known in Europe. It was first imported from the East into Venice, and then into Spain; in which country sealing-wax became the object of a considerable commerce, under the name of Spanish wax. In mediæval times the composition contained bees-wax.

If shellac be compounded into sealing-wax immediately after it has been separated by fusion from the palest qualities of stick or seed lac, it then forms a better and less brittle article than when the shellac is fused a second time. Hence sealing-wax rightly prepared in the East Indies deserves a preference over that made in other countries, where the lac is not indigenous. Shellac can be restored in some degree, however, to a plastic and tenacious state by melting it with a very small portion of turpentine. The palest shellac is to be selected for bright-coloured sealing-wax, the dark kind being reserved for black.

The following proportions may be followed for making red sealing-wax. Take 7 oz. of shellac, 4 oz. of Venetian turpentine, and 3-4 oz. of vermilion. Melt the lac in a copper pan suspended over a clear fire, then pour the turpentine slowly into it, and soon afterwards add the vermilion, stirring the mixture briskly all the time with a rod in either hand. In forming the round sticks of sealing-wax, a certain portion of the mass should be weighed while it is ductile, divided into the desired number of pieces, and then rolled out upon a warm marble slab, by means of a smooth wooden block, like that used by apothecaries for rolling a mass of pills. The oval sticks of sealing-wax are cast in moulds, with the above compound in a state of fusion. The marks of the lines of junction of the mould-box may be afterwards removed by holding the sticks over a clear fire, or passing them over a blue gas-flame. Marbled sealing-wax is made by mixing two, three, or more coloured kinds of it while they are in a semi-fluid state. From the viscosity of the several masses, their incorporation is left

incomplete, so as to produce the appearance of marbling. Gold sealing-wax is made simply by stirring gold-coloured mica spangles into the melted resins. Wax may be scented by introducing a little essential oil, essence of musk, or other perfume. If 1 part of balsam of Peru be melted along with 99 parts of the sealing-wax composition, an agreeable fragrance will be exhaled in the act of sealing with it. Either lampblack or ivory-black serves for the colouring matter of black wax. Sealing-wax is often adulterated with resin; in which case it runs into thin drops at the flame of a candle.

The following proportions are stated to form good sealing-wax:—

Red.—4 oz. turpentine, 5½ oz. shellac, 1½ oz. colophony, 1¼ oz. cinnabar, magnesia to colour.

Fine black.—4½ oz. Venetian turpentine, 9 oz. shellac, ½ oz. colophony, lampblack mixed with oil of turpentine as much as is required.

Black.—4 oz. Venetian turpentine, 8 oz. shellac, 3 oz. colophony, lampblack, and oil of turpentine.

Yellow.—2 oz. Venetian turpentine, 4 oz. shellac, 1¼ oz. colophony, ¾ oz. King's yellow.

Dark brown.—4 oz. Venetian turpentine, 7½ oz. shellac, 1½ oz. brown English earth (ochre).

Light brown.—4 oz. Venetian turpentine, 7½ oz. shellac, 1 oz. brown earth, ½ oz. cinnabar.

Dark blue.—3 oz. Venetian turpentine, 7 oz. fine shellac, 1 oz. colophony, 1 oz. mineral blue.

Green.—2 oz. Venetian turpentine, 4 oz. shellac, 1¼ oz. colophony, ½ oz. King's yellow, ¼ oz. mountain blue.

Gold.—4 oz. Venetian turpentine, 8 oz. shellac, 14 sheets of genuine leaf-gold, ½ oz. bronze, ½ oz. magnesia with oil of turpentine (Ure).

Sealing-wax that can be used without the need for a special flame in which to melt it is made by casting the sticks with a loosely woven wick running through the centre. When a light is applied to the wick it continues burning as long as required (Kressel, Eng. Pat. 13027, 1893; J. Soc. Chem. Ind. 1893, 1045).

For the preparation of the cheaper varieties of sealing-wax, used for sealing bottles, &c., the powdered ingredients may be simply mixed together and moulded into sticks under pressure, instead of being fused together (Watkins and Nunn, Eng. Pat. 15180, 1897; J. Soc. Chem. Ind. 1897, 815).

Sealing-wax that is insoluble in alcohol may be made: (1) By melting together 1 part of carnäuba wax and 1 part of hard paraffin, and adding, with constant stirring, 5 parts of red lead and 2 parts of whiting (J. Soc. Chem. Ind. 1900, 157). (2) By incorporating 3 parts of slaked lime with about 23 parts of molten colophony, thus forming calcium resinate to which is added a little heavy petroleum oil in order to render it less brittle (Ellram, Eng. Pat. 12176, 1899; J. Soc. Chem. Ind. 1900, 452).

Goldschmidt (Chem. Zeit. 1905, 29, 33) recommends the use of formaldehyde resins for preparing sealing-wax.

Elastic and flexible sealing-wax is made by mixing at 100°, 100 parts of gutta-percha or caoutchouc, 12.4 parts of lac, and 25 parts of rubber, dissolved in benzene (Schaar and Bergmeister, Fr. Pat. 391121, 1908; J. Soc. Chem. Ind. 1908, 1122).

SEAL OIL. Seal oil is obtained from the blubber of the various species of seal, such as *Phoca vitulina*, *Phoca grænder*, *Phoca lagura*, *Phoca caspica*, &c.

The following seals are caught in the Antarctic Ocean: Weddell's seal (*Leptonychotes Weddelli*), sea-leopard (*Stenorhynchus leptonyx*), crab-eating seal (*Lobodon carcinophagus*), Ross's seal (*Ommatophoca Rossi*), sea-elephant (*Macrorhinus leoninus*), Hooker's sea lion (*Arctocephalus Hookeri*).

In the early times of 'whaling,' the oil was exclusively 'tried' on board the whaling vessels, just as in the case of whale oil. Later, the seals were brought to rendering establishments on shore, and the blubber, cut from the animal, was thrown into large vessels of great height, in which the oil was pressed out from the lower layers by the superincumbent weight of the blubber, and the exuding oil was allowed to run off continuously. The oil running out at first was pale, and almost free from smell. When, however, the blubber became rancid and even putrid, the oil obtained was rich in free fatty acids, and had a dark colour and a nauseous taste and odour. At present, seal oil is recovered by more rational methods, such as will be described under the heading 'whale oil.'

The colour of seal oil varies according to whether the oil is extracted from fresh blubber on board the steamer, or from blubber which has been brought to shore.

Crude seal oils deposit 'stearine' on standing, which is removed by filtering the oil. The 'stearine' is sold as 'fish stearine' or 'fish tallow' for soap-making and currying purposes. The 'stearine' from the first run oil is white and almost free from colour, whereas the 'stearine' obtained from the last rendered oil is dark, high in its proportion of free fatty acids, and of bad odour. This 'stearine' blackens easily on exposure to the atmosphere.

In commerce we find four qualities of seal oil, which are differentiated as 'water-white,' 'straw,' 'yellow,' and 'brown' seal oil; these represent the oils as they are obtained successively from the blubber by 'rendering.' The darkest quality is that which has been the longest in contact with the animal tissue, and has been extracted at the highest temperature.

The oil from *Phoca foetida*, occurring in the Baltic, differs notably from the seal oils furnished by the marine seals in respect of the iodine value. This must be attributed to the influence of food conditioned by the fauna of an inland sea. Such influence becomes more pronounced still in the case of the seal oil from *Phoca foetida*, var. *Saimensis Nordkvist*, a variety of seal which has adapted itself for many generations to the fresh water of the Saima lake. (For the characteristics of seal oil, see OILS, FIXED, AND FATS.)

A sample of oil obtained from the blubber of a seal caught in the North Sea was of thick consistency and of dark brown colour, and had a marked fishy odour. The saponif. value was 184.6–187.3, iodine value 82.4–85.8, and $n_D^{18} = 1.4787$. The iodine value is much lower than that usually assigned to seal oils, a fact which may be accounted for by the oil having

been kept in a sealed tin for five years before examination. By bromination in ether containing glacial acetic acid, 13.3 p.c. of insoluble bromides, which blackened on heating to 222° and were otherwise similar to the octobromide of clupanodonic acid, were obtained, and 10 p.c. of insoluble fatty acids were obtained by the lead salt-benzene method. These fatty acids were liberated and fractionally crystallised, and were shown to consist entirely of palmitic acid. The lead salts soluble in benzene gave a mixture of acids of iodine value 90–93 (Hanus). This was oxidised with 2 p.c. permanganate by Hazura's method, and dihydroxypalmitic acid obtained on repeated recrystallisation from alcohol. The fatty acids present as glycerides in seal oil therefore consist of palmitic acid, the hexadecylenic acid, known as physetoleic acid, and small quantities of clupanodonic acid. The presence of physetoleic acid was confirmed by the formation of palmitic acid on hydrogenation. It is uncertain whether physetoleic acid is identical with the acid of the same formula discovered by Bull in cod-liver oil and named zoomaric acid (cf. Schmidt-Nielsen, J. 1922, 300 A), and referred to as a universal constituent of marine animal oils (K. H. Bauer and W. Neth, (Chem. Umschau, 1924, 31, 5; J. Soc. Chem. Ind. 1924, 43, B. 183).

Seal oil contains about 10 p.c. of palmitic acid and notable quantities of clupanodonic acid. The nature of the bulk of the seal oil fatty acids has not yet been fully investigated.

Seal oil is frequently adulterated with mineral oils and resin oils, the detection of which is, however, easy. A mixture of seal oil with various fish oils is frequently sold as seal oil. The detection of the adulterant is not easy, as neither the iodine value nor the bromide test furnish decisive indications. In the present state of our knowledge the taste and smell alone render some assistance in the examination.

J. L.

SEA-WOLF LIVER OIL. An oil extracted from the livers of the species *Anarrhichas lupus* (Linn.). Has a clear golden-brown colour and a curious odour unlike that of other liver oils. The oils from the male and female livers gave respectively the following characters: d_{15}^{15} 0.9162, 0.9179; n_D^{25} 1.4733, 1.4702; acid number 13.11, 14.37; saponification number 182.8, 185.2; iodine number (Wijs) 131.2, 118.1; unsaponifiable matter, 5.23, 3.86; fatty acids 92.4 p.c., 92.2 p.c.; m.p. of fatty acids 24.5°, 24.7°; mean molecular weight of the fatty acids 276.8, 279.9.

The oil is used in Russia mixed with coal-fish liver oil in tanning (Lexow, Chem. Umschau, 1921, 28, 213).

SEBACIC ACID. *Ipomic acid.* (Fettsäure. Sebacinsäure. Ipomsäure, Ger.)



Obtained by the dry distillation of oleic acid and of bodies containing oleic acid (Redtenbacher, Annalen, 35, 188); also formed when these bodies become rancid (Scala, Chem. Zentr. 1898, i. 439). Prepared by the action of caustic alkali on castor oil (Bouis, Annalen, 80, 303; 97, 34; Witt, Ber. 1874, 220); by the oxidation of spermaceti, stearic acid (Arppe, Zeitsch. Chem. 1865,

296), jalapin or jalapinic acid (Mayer, *Annalen*, 83, 143; 95, 160; Neison and Bayne, *J.* 1874, 625) with nitric acid; by the electrolysis of an aqueous solution of the potassium salt of the monoethyl ester of suberic acid and hydrolysing the diethyl ester thus formed (Brown and Walker, *Annalen*, 261, 121); by treating the condensation product of dibromobutane and magnesium with carbon dioxide (Gauthier, *Ann. Chim.* [viii.] 16, 350); also obtained from shellac (Endemann, *Chem. Zentr.* 1908, i. 1861). Has been synthesised from ethyl sodiomalonate and hexamethylene dibromide (Haworth and Perkin, *Chem. Soc. Trans.* 1894, 600). Sahlfield (*Eng. Pat.* 18940; *J. Soc. Chem. Ind.* 1896, 909) prepares sebacic acid by distilling wool grease or fulling grease from a retort, superheated to 300°, steam being injected into the neck of the retort. Sebacic acid crystallises in colourless nodular masses, m.p. 129° (Massol, *Bull. Soc. chim.* [iii.] 17, 746); readily soluble in alcohol or ether, sparingly soluble in water. On oxidation with nitric acid or permanganate, adipic, glutaric, and succinic acids are produced, together with a small quantity of γ -heptanone- $\alpha\eta$ -dicarboxylic acid (Arppe, *l.c.*; Carotte, *Bull. Soc. chim.* [ii.] 45, 270; Bödtker, *J. pr. Chem.* 1912, [ii.] 85, 221). By heating the acid with lime, sebacin $C_{10}H_{18}$, valeraldehyde and α -naphthol are produced (Calvi, *Annalen*, 91, 110; Petersen, *ibid.* 103, 184). The anhydride melts at 78°–79° (Anderlini, *Ber.* 1894, Ref. 405). The esters of sebacic acid can be used in the manufacture of celluloid (Goldsmith and British Xylonite Co., *D. R. P.* 139738; *Chem. Zentr.* 1903, i. 749).

Sebacic acid gives a precipitate with a neutral solution of a thorium salt, a reaction which can be employed for the separation and estimation of thorium (Smith and James, *J. Amer. Chem. Soc.* 1912, 34, 281).

Compounds of sebacic acid with other rare earths have been described by Whittemore and James (*J. Amer. Chem. Soc.* 1913, 35, 127).

E. Bödtker (*J. Pharm. Chim.* 1924, 29, 313) confirms the work of Bouis (*Compt. rend.* 1855, 41, 603; *Ann. Chim.* 1855, 44, 77), who showed that ricinoleic acid (100 grms.) on distillation with an excess of caustic soda gave sebacic acid (25 grms.), octyl alcohol (20 grms., mixed with isomeric methyl hexyl ketone), and a viscous brown residue. From the latter have now been isolated stearic acid, an acid of m.p. 81°–82°, which is either ricinic acid, $C_{18}H_{34}O_3$ (*cf.* Krafft, *J. Chem. Soc.* 1888, ii. 1270; Walden, *J. Chem. Soc.* 1895, i. 125), or hydroxystearic acid, $C_{18}H_{36}O_3$, undecylenic acid, $C_{11}H_{20}O_2$, formed by pyrogenic decomposition of the ricinoleic acid, and an asphaltic resin. The maximum yield of sebacic acid (33 grms. from 100 grms. of ricinoleic acid) is obtained by heating sodium ricinoleate with the equivalent of caustic soda (*J. Soc. Chem. Ind.* 1924, 43, B. 478).

SECALE CORNUTUM, SECALE-AMINO SULPHONIC ACID, SECALONIC ACID *v.* **ERGOT.**

SECLOHEPTOSE. A non-fermentable heptose found in the leaves and stems of the stone crop, *Sedum spectabile* (La Forge and Hudson, *J. Biol. Chem.* 1917, 30, 61).

SECRETAGE. A process in which mercury

or some of its salts is employed to impart to the fur of animals the property of felting.

SECURITE *v.* **EXPLOSIVES.**

SEED LAC *v.* **RESINS.**

SEID OIL. An oil contained in the rhizomes of *Cyperus rotundus* (Linn.), a glabrous herb growing freely throughout the Sudan. The oil has an aromatic, camphoraceous odour, and has the following constants: d_{20}^{26} 0.9548, α_{25}^{25} –19.9°, n_{25}^{25} 1.4967, acid number 1.0, sapon. number 6.6, ditto after acetylation 105 (corresponding with 45 p.c. of alcohol). Solubility in 80 p.c. alcohol 1 in 4. Insoluble in 70 p.c. alcohol (Joseph and Whitfield, *J. Soc. Chem. Ind.* 1922, 41, 172 T).

SEIGNETTE'S SALT. (*Potassium sodium tartrate* $C_4H_4O_6KNa \cdot 4H_2O$ or *Rochelle salt*.) So named from having been discovered by Seignette, an apothecary in Rochelle, in 1672.

SELENITE. *Hydrated calcium sulphate* (*v.* **CALCIUM**; also **GYP SUM**).

SELENIUM. Sym. Se. At.wt. 79.7 (Petersson and Ekman, Lenher, Meyer, Kužma and Křehlik (*Trans. Boherman Acad.* 19 (2), 3); Tannek and Meyer (*Zeitsch. anorg. Chem.* 1913, 83, 51); Bruylants and Bytebier (*Bull. Acad. Belg.* 1912, 856, 79, 18); Bruylants and Dondeyne (*Bull. Acad. roy. Belg.* 1922, [v.] 8, 387); see also Olivari (*Atti R. Accad. Lincei*, 1908, [v.] 17, ii. 389; 1909, 18, i. 465; ii. 94, 264). According to Aston, selenium consists of six isotopes, giving lines at 80, 78, 76, 82, 77 and 74 respectively, in decreasing order of intensity. This element was discovered by Berzelius in 1817 in the deposit of a sulphuric acid manufactured at Gripsholm, and is widely distributed in small quantities. It occurs native in cavities in Vesuvian lavas. In combination it is found as *sulphur selenide* or *selenium sulphur* in native sulphur; as *clausthalite* $PbSe$, *lehrbachite* $PbSe, HgSe$, *onofrite* $HgSe, 4HgS$, *eucairite* $CuSe, Ag_2Se$, *crookesite* $(CuTlAg)Se$, and other minerals. It occurs in many varieties of copper and iron pyrites, especially in Norwegian pyrites, and is precipitated from the sulphuric acid prepared from them. It has been found by H. N. Warren in meteoric iron, and in the mineral waters from La Roche-Posay (Taboury, *Bull. Soc. chim.* 1909, [iv.] 5, 865).

For double selenides, see Meyer and Bratke (*Zeitsch. anorg. Chem.* 1924, 135, 289; *Chem. Soc. Abstr.* 1924, 126, ii. 550).

Selenium may be prepared from the deposit from sulphuric acid in the chambers and Glover towers. The deposit is boiled with concentrated sulphuric acid and a quantity of sodium nitrate corresponding with the amount of selenium. The mixture is then diluted, stirred, and steam is blown through it till the sp.gr. is 1.25, the remaining oxides of nitrogen being expelled by a stream of air. The solution is filtered and the filtrate and washings are boiled with hydrochloric acid, after which the selenium is precipitated by a stream of purified sulphur dioxide. After washing and drying 99 p.c. selenium is obtained (Littmann, *Zeitsch. angew. Chem.* 1906, 19, 1081). Instead of sodium nitrate, potassium permanganate and sodium chloride may be used (Koch, *D. R. P.* 167457, 1903; *J. Soc. Chem. Ind.* 1906, 1220).

By a second method the chamber deposit is heated with concentrated potassium cyanide

solution until it becomes grey. The solution, containing potassium selenocyanate, is filtered and treated with hydrochloric acid and sulphurous acid. The selenium is best purified by evaporation to dryness with nitric acid, subliming the selenious oxide so formed in a current of air and then dissolving it in water and precipitating selenium by means of hydrochloric acid and sulphur dioxide, the process being repeated several times (Threlfall, Proc. Roy. Soc. 1907, A, 79, 167; Dennis and Koller, J. Amer. Chem. Soc. 1919, 41, 949).

Selenium, like sulphur with which it is isomorphous, exists in different allotropic forms (Coninck, Compt. rend. 1906, 142, 571; 143, 682; Coninck and Raynaud, Bull. Acad. Roy. Belg. 1907, 365; 1908, 57).

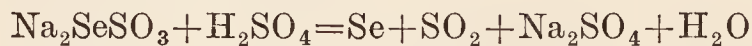
Amorphous selenium is formed as a finely divided brick-red powder when a solution of selenious acid is precipitated by sulphur dioxide gas, or when the acid is reduced by zinc, stannous chloride, or other reducing agents. It has a sp.gr. 4.26, and is soluble in carbon disulphide.

Semicolloidal red amorphous selenium is formed when solutions of dextrose and selenious or selenic acid are gently heated together. At 100° it is partially transformed into ordinary black selenium (Coninck and Chauvenet, Compt. rend. 1905, 141, 1234).

Colloidal selenium can also be obtained by dissolving in water the red selenium obtained by the reduction of selenium dioxide. The solution is blood-red, but assumes an orange-tint when sufficiently diluted with water.

It is formed by dissolving the element in hydrazine hydrate and pouring into water at ordinary temperature.

It may also be prepared by the action of dilute sulphuric acid on very dilute solutions of sodium selenosulphate:



On filtration through a Zsigmondy ultra-filter the dark-red liquid gives colourless solutions which are stable (Meyer, Z. Elektro-chem. 1919, 25, 80).

Similar solutions are produced by the reduction of selenious acid in aqueous sodium protalbate or lysalbate with hydrazine hydrate or hydroxylamine hydrochloride. The precipitate is then dissolved in sodium carbonate and the solution dialysed. On gentle evaporation, stable red glistening flakes, completely soluble in water, are obtained (Paal and Koch, Ber. 1905, 38, 526). For other methods of producing colloidal selenium, see Dittmar, Chem. Zentr. 1905, ii. 741; Müller and Nowakowski, Ber. 1905, 38, 3779; Gutbier and Lohmann, Zeitsch. anorg. Chem. 1904, 42, 325; 1905, 43, 384; D. R. P. 164664, 1904; Gutbier and Heinrich, Koll. Chem. Beihefte, 1913, 4, 411; Gutbier and Engeroff, Kolloid. Zeitsch. 1914, 15, 193, 210; Gutbier and Emslander, Ber. 1921, 54, 1974; Gutbier and Weise, *ibid.* 1919, 52, [B], 1374.

Vitreous selenium is formed when the amorphous variety is heated to 217° and then rapidly cooled. It forms a brownish-black, brittle, glassy mass of sp.gr. 4.28, soluble in carbon disulphide. Like the ordinary amorphous selenium it does not conduct electricity. These three forms are generally regarded as all belonging to one allotropic modification and are some-

times known as 'liquid' selenium (Saunders, J. Phys. Chem. 1900, 4, 423). If vitreous selenium melted at 220° is cooled rapidly under pressure it is transformed into a violet-grey modification, formed of slender crystals, very sensitive photo-electrically, but very unstable (Angel, *v. infra*).

The red crystalline form soluble in carbon disulphide, separates out when the latter is put into contact with amorphous selenium. This variety exists in two modifications, both belonging to the monoclinic system.

Metallic selenium is obtained when melted selenium is cooled quickly to 210° and then maintained at that temperature for some time (Littmann, *l.c.*; Marc, Ber. 1906, 39, 697), by placing amorphous selenium in contact with aniline or quinoline (Schrott, Chem. Zeit. 1906, 30, Rep. 384), or by fusing the vitreous form between carbon plates and then allowing to cool slowly (Coste, Compt. rend. 1905, 141, 715). When a solution in potassium hydroxide at 230° is allowed to cool slowly metallic selenium separates out in long needles, sp.gr. 4.82, and m.p. 219° (Coste, Compt. rend. 1909, 149, 674). Other varieties of metallic selenium melt at 210° and at 217°. Metallic selenium is more stable and less chemically active than the amorphous or red crystalline forms.

Grey crystalline metallic selenium also occurs in two modifications. One, A, forms round granular crystals stable at 140°, and in the dark, is a non-conductor of electricity; the other, B, formed when A is heated to 200° for some time or is exposed to light, forms longer crystals somewhat less soluble in carbon disulphide, and is a good conductor of electricity (Marc, Zeitsch. anorg. Chem. 1903, 37, 459; 1907, 53, 298; Ries, Physik. Zeitsch. 1908, 9, 228; Kruyt, Zeitsch. anorg. Chem. 1909, 64, 305).

The thermal conductivity of vitreous selenium at 25° lies between 0.000293 and 0.000328; that of crystalline selenium at 25° varies from 0.00070 to 0.00183 (Sayce, J. Proc. Roy. Soc. N. S. Wales, 1917, 51, 356).

The electrical resistance of selenium is, in general, increased when heated and diminished considerably on exposure to light, the action being principally produced by the red rays (Marc, Zeitsch. anorg. Chem. 1906, 48, 393; 50, 446; and *l.c.*; Hesehus, Chem. Zentr. 1906, i. 1080). The change of conductivity is instantaneous, and is almost double in sunlight, but even the light from a small lamp has a noticeable effect. The resistance gradually returns after removal from light. On this property depends the construction of the *photophone*, in which light is converted into electricity (Carpini, Atti R. Accad. Lincei, 1905, [v.] 14, 667).

For theories as to the cause of the sensitiveness of selenium preparations to light, see Ries, Physikal. Zeitsch. 1911, 12, 480; Pochettino, Nuovo Cim. 1912, [vi.] 4, 189.

For the use of selenium cells for spectrophotometric purposes generally, see Bloch, Compt. rend. 1901, 132, 914; Torda and Bornand, Eng. Pat. 4020, 1905; J. Soc. Chem. Ind. 1906, 91; Marc, *l.c.*; 1903, 37, 459; Angel, Bull. Soc. Chem. 1915, [iv.] 17, 10.

A. Weinhold (Dingl. poly. J. 239, 160) has described the preparation of selenium resistance rods for photophonic purposes.

The electrical resistance of selenium is diminished by radium and Röntgen rays, and by the proximity of turpentine, of hydrogen peroxide (Bloch, *l.c.*; Aubel, *Compt. rend.* 1903, 136, 929), and of various pigments (Griffiths, *ibid.* 1903, 137, 647).

Selenium has also been used for observations of the transit of Venus and of the sun's eclipse.

Selenium has been employed in the production of coloured glass, a rose tint being obtained by the direct addition of selenium to the melting-pot. An orange-red colour is produced when cadmium sulphide is mixed with the selenium before adding the latter to the molten glass (*Eng. & Mining J.* Dec. 18, 1897, 731). Glasses which contain molecular disperse selenium in the form of polyselenides have a chestnut-brown colour; those which contain colloidal selenium vary from yellow to reddish-violet (Fenaroli, *Kolloid. Zeitsch.* 1915, 16, 53).

Selenium melts at 217° and boils at 690° at 760 mm. (Berthelot, *Compt. rend.* 1902, 134, 75). The vapour becomes pale yellow at 600° ; between 600° and 700° it is deep orange; at 850° it again becomes pale yellow, and no further change occurs at higher temperatures (Dobbie and Fox, *Proc. Roy. Soc.* 1920, 147). According to Preuner and Brockmüller (*Zeitsch. physikal. Chem.* 1912, 81, 129) the selenium mol. approaches Se_6 at the lowest temperatures and Se_2 at the highest. In a high vacuum it boils at 310° (Krafft, *Ber.* 1903, 36, 1690, 4344).

Molecular weight.—The molecular weight of selenium in iodine has been found (Olivari, *Chem. Soc. Abstr.* 1909, ii. 39) to be Se_2 instead of Se_8 , whilst there is no indication of the presence of a compound (Pellini and Pedrina, *Chem. Soc. Abstr.* 1908, ii. 833). The low molecular weight is confirmed, and is almost the same at 184° as at 104° . Under similar conditions sulphur gives values falling little below S_8 .

Anthraquinone (cryoscopic constant 148) gives S_8 and Se_8 , whilst diphenyl (ebullioscopic constant 59.3) gives similar values. It is therefore a specific influence of the iodine, and not of high temperature, that causes the dissociation of the selenium molecule.

Selenium reacts with iodine, and the cryoscopic and ebullioscopic results indicate a large proportion of single atoms (Beckmann and Hanslian, *Zeitsch. anorg. Chem.* 1912, 80, 221; *Chem. Soc. Abstr.* 1913, ii. 402).

For observations on the molecular weight of selenium in solution, see Olivari, *Atti R. Accad. Lincei*, 1912, [v.] 21, i. 718; Beckmann, *K. Akad. Berl.* 1913, 886.

Selenium is odourless and tasteless, but the vapour possesses an odour of putrid horseradish. It burns with a reddish-blue flame. In cold concentrated sulphuric acid it dissolves with a fine green colour, with formation of selenosulphur trioxide SeSO_3 , from which solution selenium is precipitated by water. Its presence in commercial sulphuric acid may be detected by heating the acid with a crystal of aspidospermine when a deep violet colour is produced. It mixes in all proportions with sulphur, crystals containing both elements in varying proportions being deposited from their solution in carbon disulphide (Rathke, *Ber.* 1903, 36, 594). It can form phosphorescent preparations with the

alkaline earths (Pauli, *Ann. Physik.* 1912, [iv.] 33, 870). Selenium can also replace sulphur in alums and in many organic compounds (Gutbier, *Zeitsch. anorg. Chem.* 1902, 32, 257; Frerichs, *Arch. Pharm.* 1903, 241, 177; Coos, *Ber.* 1902, 35, 4109; Chabrie and Bouchonnet, *Compt. rend.* 1903, 136, 376; Stollé and Gutmann, *J. pr. Chem.* 1904, ii. 69, 509; Becker and Meyer, *Ber.* 1904, 37, 2550; Edinger and Ritsema, *J. pr. Chem.* 1903, [ii.] 68, 72; Scott, *Chem. Soc. Proc.* 1904, 156; Smiles and Hilditch, *ibid.* 1907, 12; Michäelis, *Annalen*, 1905, 338, 267; 1907, 352, 152; Frerichs and Wildt, *ibid.* 1908, 360, 105; Simon, *Monatsh.* 1905, 26, 959; Taboury, *Bull. Soc. chim.* 1906, [iii.] 35, 668; Krafft, *Ber.* 1906, 39, 2197; Tschugaeff, *ibid.* 1909, 42, 49; Doughty, *Amer. Chem. J.* 1909, 41, 326; Gassmann, *Zeitsch. physiol. Chem.* 1917, 100, 209).

Selenoantipyrin $\text{C}_{11}\text{H}_{12}\text{N}_2\text{Se}$ is prepared by treating antipyrin hydrochloride with potassium selenide or hydroselenide. It forms light yellow glistening crystals, m.p. 168° (Michäelis, *Zeitsch. angew. Chem.* 1901, 14, 1027; *Annalen*, 1902, 320, 1).

Selenium combines directly with many metals forming selenides; it reduces silver chloride in the cold, and gold compounds when heated to boiling, the metallic selenides being formed (Hall and Lenher, *J. Amer. Chem. Soc.* 1902, 24, 918).

Seleniuretted hydrogen SeH_2 is produced by the action of dilute hydrochloric acid on ferrous or alkaline selenide, or better by the action of water on aluminium selenide Al_2Se_3 , or magnesium selenide MgSe , or by heating selenium in hydrogen gas, the quantity produced depending in the latter case upon the temperature. It decomposes when heated, so that when selenium is heated in hydrogen in a glass tube the hydride is at first produced, and is again reduced with deposition of crystalline selenium on the colder parts of the tube (Troutman, *Bull. Soc. Ind. Mulhouse*, 1891, 87; Pélabon, *Compt. rend.* 1894, 118, 142; 1894, 119, 73; 1895, 121, 401; 1897, 124, 360; Bodenstein, *Zeitsch. physikal. Chem.* 1899, 29, 429; Jones, *Mem. Manch. Phil. Soc.* 1904, 48, 1).

It is a colourless poisonous gas of persistent foetid odour, more soluble in water than sulphuretted hydrogen, the solution being acid to litmus and absorbing oxygen from the air, with deposition of red selenium. It precipitates most heavy metals as selenides. The gas condenses to a liquid, b.p. -42° , which solidifies at -64° . One litre at n.t.p. weighs 3.6715 grms. (Bruylants and Bytebier, *Bull. Acad. Roy. Belg.* 1912, 856). It is not sensitive to daylight, but is decomposed by ultra-violet light. Dry oxygen has no action on the dry gas, but in presence of moisture it is rapidly decomposed.

For its electrolytic dissociation, see De Hlasko, *J. Chim. Phys.* 1923, 20, 167. For its viscosity and molecular dimensions, see C. J. Smith, *Trans. Faraday Soc.* 1923, 18, 302.

Selenium forms an oxide SeO_2 , produced by evaporating selenium with nitric acid (Krafft and Steiner, *Ber.* 1901, 34, 560), or by heating the metal in dried oxygen, in white needle-shaped hygroscopic crystals, which sublime unmelted at about 300° , forming a yellow vapour (Coninck, *Compt. rend.* 1906, 142, 571; Meyer,

Ber. 1922, 55, 2082). This, when introduced into a Bunsen flame, gives an intense blue colour and deposits selenium on a cold surface. It forms a hydrate $\text{SeO}_2 \cdot \text{H}_2\text{O}$.

Selenium dioxide yields yellow crystalline additive compounds with tetraethyl- and tetramethyl-ammonium chlorides such as



(Carnevali, Atti R. Accad. Lincei, 1908, [v.] 17, ii. 385).

According to von Konek (Ber. 1918, 51, 872) Se_3O_4 also exists. It is almost insoluble in water and is decomposed by boiling sodium hydroxide, about one-third of the selenium being deposited as such, the rest forming sodium salts of selenium acids.

Selenium trioxide is prepared by prolonged treatment of selenium in solution in selenium oxychloride with dry ozone. The selenium trioxide is obtained as a white solid mixed with some oxychloride, from which it can be freed by washing first with carbon tetrachloride and then with ether. The trioxide is a pale yellow amorphous solid, d 3.6, decomposing at 120° without melting or subliming, and soluble in water (to form selenic acid) and alcohol, but insoluble in ether, carbon tetrachloride, chloroform, and benzene. It dissolves in alkalis to form selenates. The trioxide combines with dry hydrogen chloride with considerable evolution of heat, forming chloroselenic acid, a fuming, colourless liquid. Decomposition and separation of selenium occur if the temperature is not kept low during the preparation. Chloroselenic acid, probably $(\text{HClSeO}_3)_2$, d 2.26, solidifies at -46° , and decomposes on heating, giving hydrochloric acid, selenium dioxide, and selenium. It dissolves readily in water, forming hydrochloric and selenic acids, and in selenium oxychloride, and is decomposed by alcohol with precipitation of selenium. Selenium trioxide and chloroselenic acid both react with hydrogen peroxide to form a perselenate. They appear to be analogous in all respects to the sulphur compounds, but less stable (R. R. Le G. Worsley and H. B. Baker, Chem. Soc. Trans. 1923, 123, 2870; J. Soc. Chem. Ind. 1924, 43, B. 93).

The solubility of a number of anhydrous metallic chlorides in selenium oxychloride has been determined, and the following double compounds have been isolated: $\text{TiCl}_4 \cdot 2\text{SeOCl}_2$; $\text{SnCl}_4 \cdot 2\text{SeOCl}_2$; $\text{SbCl}_5 \cdot 2\text{SeOCl}_2$; $\text{FeCl}_3 \cdot 2\text{SeOCl}_2$; $\text{KCl} \cdot \text{SeOCl}_2$; $\text{RbCl} \cdot \text{SeOCl}_2$; $\text{CaCl}_2 \cdot 3\text{SeOCl}_2$; $\text{MgCl}_2 \cdot 3\text{SeOCl}_2$ (C. R. Wise, J. Amer. Chem. Soc. 1923, 45, 1233).

Selenious acid H_2SeO_3 is produced by solution of selenium in nitric acid or of selenious oxide in hot water. It crystallises from solution in colourless prisms.

It is reduced by many organic substances, by sulphur dioxide in the presence of acid, or when exposed to the air, red selenium being formed (Coninck and Chauvenet, Bull. Acad. Roy. Belg. 1906, 81; Chabré and Lapicque, Compt. rend. 1890, 110, 152).

A number of acid and neutral selenites are known. They are very poisonous and all evolve selenium when heated with ammonium chloride in a tube, or when acted on by certain moulds and bacteria (Gosio, Atti Roy. Accad. Lincei,

1904, [v.] 13, i. 642), producing the horse-radish smell when heated on charcoal in the reducing flame owing to the formation of a carbon diselenide (Rathke, Ber. 1903, 36, 600).

Thiocyanoselenious acid $(\text{HCNS})_2\text{H}_2\text{SeO}_3$ is described by Iwanoff (Chem. Zeit. 1908, 32, 468).

Selenic acid H_2SeO_4 may be produced by the action of chlorine, bromine, hydrogen peroxide, or chloric acid on aqueous selenious acid. When selenites are similarly treated, selenates are produced.

Selenic acid is conveniently prepared by electrolysing a solution of selenious acid at 50° – 60° , containing an excess of nitric acid and employing a current of 4–5 ampères per square cm. for about 100 c.c. of solution (Glausner, Chem. Zeit. 1907, 31, 630; Manuelli and Lazzarini, Gazz. chim. ital. 1909, 39, i. 50). Also by the electrolysis of lead selenate (Mathers, J. Amer. Chem. Soc. 1908, 30, 1374), or copper selenate (Metzner, Compt. rend. 1898, 127, 54). It cannot be obtained in the anhydrous condition by evaporation in air as it decomposes into oxygen, water, and selenious oxide at 280° . But if heated in a vacuum to 180° and then cooled, the product solidifies to a crystalline mass consisting of the pure acid (Cameron and Macallan, Chem. News, 1889, 59, 219). It melts at 58° ; like sulphuric acid it chars organic matter, and combines eagerly with water forming a *monohydrate*, m.p. 26° , and also a *tetrahydrate*. Aqueous solution of this acid dissolves gold, copper, iron, and other metals, forming selenates, which closely resemble sulphates (Lenher, J. Amer. Chem. Soc. 1902, 24, 354; Tutton, Proc. Roy. Soc. 1918, A, 94, 352; Dennis and Koller (*l.c.*). For complex selenates *v.* Meyer, Zeitsch. anorg. Chem. 1921, 118, 1); they are all reduced to selenites when heated with hydrochloric acid.

Selenic acid is reduced to selenium by formic, oxalic, malonic or pyruvic acid, and also by various aldehydes (Coninck and Chauvenet, *l.c.* 601).

Nitrogen tetroxide reacts with a concentrated solution of selenic acid cooled with solid carbon dioxide, forming the compound



(Erdmann, Ber. 1906, 39, 1207).

Acids containing both sulphur and selenium are also known, as *selenosulphuric acid* H_2SeSO_3 and *selenotriithionic acid* $\text{H}_2\text{SeS}_2\text{O}_6$.

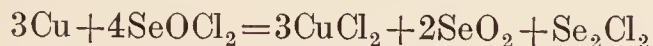
Selenium forms two *chlorides* and an *oxychloride* Se_2Cl_2 , SeCl_4 , SeOCl_2 (Lamb, Amer. Chem. J. 1903, 30, 209; Lenher and North, J. Amer. Chem. Soc. 1907, 29, 33; Lenher, *ibid.* 1920, 42, 2498; 1921, 43, 29; 1922, 44, 1664), and the corresponding *bromides*, an *oxybromide*, a reddish-yellow solid, m.p. 41.5° – 41.7° , boiling at 217° at 740 mm. (decomposition), forming selenious and hydrobromic acids on treatment with water; soluble in carbon bisulphide, chloroform, and aromatic hydrocarbons (Lenher), and two *chlorobromides* SeClBr_3 and SeBrCl_3 ; but, according to Pellini and Pedrina (Atti R. Accad. Lincei, 1908, [v.] ii. 78; 1909, [v.] 18, i. 463), selenium does not form compounds with iodine. Cf. Beckmann and Faust, Zeitsch. anorg. Chem. 1913, 84, 103; Wright, Chem. Soc. Trans. 1915, 107, 1527.

It forms complex compounds with the

halogens and sulphur (Prandtl and Borinski, *Zeitsch. anorg. Chem.* 1909, 62, 237).

For the solubilities of certain metallic chlorides in selenium oxychloride, see Clarence R. Wise, *J. Amer. Chem. Soc.* 1923, 45, 1233.

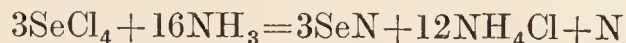
Selenium oxychloride reacts with metallic copper at ordinary temperature, forming a black substance which is a mixture of cuprous and cupric selenides. On continued action the selenides are converted into anhydrous cupric chloride



Anhydrous cupric chloride reacts with selenium oxychloride to form a green crystalline acid selenite. Silver is changed successively into the selenide and chloride by the same reagent. The oxides of copper, silver, lead, nickel, cobalt, iron, antimony, bismuth, and tin are converted into chlorides by the action of selenium oxychloride, and selenium dioxide is formed (W. L. Ray, *J. Amer. Chem. Soc.* 1923, 45, 2090-2094; *J. Soc. Chem. Ind.* 1923, 42, 1129, A).

Selenium tetrafluoride SeF_4 is produced by the action of fluorine on selenium in a metal vessel. It is a colourless liquid boiling above 100° and solidifying at -80° . It is decomposed by water forming hydrofluoric and selenious acids and attacks glass rapidly (Lebeau, *Compt. rend.* 1907, 144, 1042). According to Prideaux (*Chem. Soc. Trans.* 1906, 320) a hexafluoride also exists (Lebeau, *l.c.*; and 1347; Ramsay, *Compt. rend.* 1907, 144, 1196).

Selenium nitride SeN or Se_4N_4 , an amorphous, pale orange-yellow, extremely explosive powder obtained by the action of gaseous ammonia on a number of compounds of selenium. Best prepared by the action of liquid ammonia on selenium dichloride or tetrachloride in presence of carbon disulphide



It is considerably more sensitive than mercury fulminate to shock or blow, and explodes when heated at 160° (Strecker and Claus, *Ber.* 1923, 56, [B] 362).

Bartal (*Chem. Zeit.* 1906, 30, 810, 1044) has prepared a number of carbon compounds of selenium by the action of carbon tetrabromide on the latter, namely SeC_4 ; Se_2C_5 ; and also $\text{Se}_4\text{C}_9\text{Br}_2$; $\text{Se}_5\text{C}_{10}\text{Br}$; $\text{Se}_3\text{C}_3\text{Br}_3\cdot 3\text{H}_2\text{O}$; $\text{Se}_2\text{C}_3\text{Br}_2$ and $\text{Se}_4\text{C}_2\text{Br}_2$. The carbide CSe is also known.

Potassium selenocyanide is best prepared by mixing 70 grms. of pure potassium cyanide with 79 grms. of finely powdered commercial selenium, and fusing the whole at the lowest possible temperature. The mass is then digested on the water-bath for 3-4 hours with frequent additions of water, after which the resulting liquor is evaporated nearly to dryness and the residue dissolved in alcohol. Carbon dioxide is passed through the solution for about 2 hours, after which the liquid is filtered, the alcohol distilled off and the selenocyanide crystals are separated from their mother-liquor by means of the filter pump (Schröder, *Ber.* 1900, 33, 1765).

Cyanogen triselenide is best prepared by spreading out potassium selenocyanide in a flat glass basin and mixing it with a third or half its weight of water, the pasty mass is stirred and a stream of nitrogen dioxide is passed through it, cyanogen and hydrogen cyanide being evolved during the whole process. The

vessel should be surrounded by ice, and after the operation is about half completed small quantities of fuming nitric acid should be added from time to time. The product consists of a mixture of potassium nitrate and cyanogen selenide, the latter being removed by treatment with pure boiling benzene, which, on cooling, deposits the triselenide as yellow plates or prismatic needles, m.p. 132° . At 148.5° the triselenide decomposes with separation of selenium. It is decomposed by water and reacts vigorously with many organic substances, especially such as contain a labile hydrogen atom (Schröder, *Ber.* 1900, 33, 1765).

Nitrosylselenic acid $\text{NO}\cdot\text{O}\cdot\text{SeO}_2\cdot\text{OH}$ is a colourless crystalline snow-like mass obtained by the action of liquid nitrogen trioxide on ice-cold, anhydrous selenic acid. It has m.p. 80° (decomp.). It is somewhat unstable even at the atmospheric temperature, and is immediately decomposed by water (Meyer and Wagneir, *Ber.* 1922, 55, [B] 690).

The following substituted aromatic selenium compounds are known (Pyman, *Chem. Soc. Trans.* 1919, 115, 166).

Phenylselenious acid PhSeO_2H . Best obtained by the action of hydrochloric acid on phenylselenic acid resulting from the interaction of selenic acid and benzene (Doughty, *Amer. Chem. J.* 1909, 41, 326; Stoecker and Krafft, *Ber.* 1906, 39, 2197). Sandy yellow grains, m.p. 124° - 125° .

Sodium phenylselenite $\text{PhSeO}_2\text{Na}\cdot 2\text{H}_2\text{O}$. Colourless plates, readily soluble in water.

Phenylselenic acid PhSeO_3H . By oxidising diphenyl selenide with moist chlorine (Stoecker and Krafft, *l.c.*; Doughty, *l.c.*).

Potassium phenylselenate $\text{PhSeO}_2\text{K}\cdot 2\text{H}_2\text{O}$. Colourless prismatic needles, readily soluble in water. The sodium salt contains 3 mols. water, clear oblong plates, readily soluble in water.

m-Nitrophenylselenious acid $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{SeO}_2\text{H}$. Obtained by the action of fuming nitric acid at 150° on phenylselenious acid, or, better, by acting with nascent nitric acid from nitre and sulphuric acid. Yellow prismatic needles; m.p. 156° - 157° (corr.); sparingly soluble in cold water, readily soluble in boiling water.

m-Nitrophenylselenic acid $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{SeO}_3\text{H}$. Obtained as the potassium salt by dissolving m-nitrophenylselenious acid in dilute solution of potassium hydroxide and treating with potassium permanganate. On filtering off the manganese dioxide, and concentrating the filtrate the potassium salt crystallises out.

Potassium m-nitrophenylselenate



Anhydrous, hard, yellow needles, readily soluble in hot, sparingly so in cold, water; explodes violently at 330° .

Barium m-nitrophenylselenate



Obtained by adding barium chloride to a solution of the potassium salt. Colourless leaflets readily soluble in hot water, sparingly soluble in cold water.

m-Nitrophenylselenic acid is obtained by treating the barium salt with sulphuric acid, and evaporating the filtered solution to a syrup. Colourless plates containing $2\text{H}_2\text{O}$. Anhydrous acid melts at 146° (corr.).

Di-m-nitrophenyl diselenide $(\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{Se})_2$. Obtained by adding a solution of sodium hydrogen sulphite to a hot aqueous solution of m-nitrophenylselenious acid. Yellow spears, m.p. 83° (corr.), insoluble in water, soluble in alcohol and ether.

Di-m-aminophenyl diselenide hydrochloride $\text{C}_{12}\text{H}_{12}\text{N}_2\text{Se}_2 \cdot 2\text{HCl}$. Prepared by adding di-m-nitrophenyl diselenide to a hot solution of sodium sulphide in dilute caustic soda, and after boiling under a reflux condenser, adding hydrochloric acid, filtering from the precipitated sulphur, adding sodium carbonate and extracting with ether, and adding dilute hydrochloric acid to the residue after distilling off the ether. Yellow needles, m.p. 291° – 292° (decomp.). Readily soluble in hot, sparingly soluble in cold dilute hydrochloric acid.

Di-m-acetylaminophenyl diselenide
 $(\text{CH}_3 \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{Se})_2$.

Obtained by the action of acetic anhydride upon di-m-aminophenyl diselenide. Short yellow needles, m.p. 185° – 186° (corr.). Insoluble in water, readily soluble in hot alcohol or glacial acetic acid.

m-Acetylaminophenylselenious acid
 $\text{CH}_3 \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{SeO}_2\text{H}$.

Prepared by hydrolysing the nitrate of m-acetylaminophenylselenious acid, formed by adding di-m-acetylaminophenyl diselenide to strong nitric acid. Slender colourless needles, m.p. 209° (decomp.). Sparingly soluble in water. The sodium salt, $\text{C}_8\text{H}_8\text{O}_3\text{NNaSe} \cdot 7\text{H}_2\text{O}$, forms microscopic needles, readily soluble in water.

Barium m-acetylaminophenylselenate
 $\text{C}_{16}\text{H}_{16}\text{O}_8\text{N}_2\text{BaSe}_2 \cdot 4\text{H}_2\text{O}$.

Colourless, flat needles, soluble in water.

Sodium m-acetylaminophenylselenate
 $\text{C}_8\text{H}_8\text{O}_4\text{NNaSe}$.

Prepared by adding sodium sulphate to a solution of the barium salt. Prismatic needles from alcohol. Readily soluble in water and alcohol.

m-Aminophenylselenic acid
 $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{SeO}_3\text{H}$.

Obtained by the action of sulphuric acid on barium m-acetylaminophenylselenate, filtering and evaporating the filtrate under diminished pressure. Colourless needles, containing $2\text{H}_2\text{O}$. After drying at 100° , m.p. 229° (decomp.). Readily soluble in hot, sparingly so in cold, water.

Sodium-m-aminophenylselenate
 $\text{C}_6\text{H}_6\text{O}_3\text{NNaSe} \cdot 3\frac{1}{2}\text{H}_2\text{O}$

forms plates, readily soluble in cold water.

When a slow current of ethylene is passed into selenium monochloride, *s-tetrachlorodiethylselenide* or $\beta\beta'$ -*dichloroethyl selenide dichloride* $(\text{CH}_2\text{Cl} \cdot \text{CH}_2)_2\text{SeCl}_2$ (Bausor, Gibson, and Pope, Chem. Soc. Trans. 1920, 117, 1453) is formed. White, needle-shaped crystals, m.p. 122.5° (m.p. 118° decomp., Heath and Semon, J. Ind. Eng. Chem. 1920, 12, 1100).

Methyl selenate Me_2SeO_4 , a yellow liquid, d^{25}_4 1.652, n 1.4316, prepared by the action of methyl iodide on silver selenate. Decomposes on distillation and deposits selenium at atmospheric temperature. Readily hydrolysed by aqueous acids or alkalis.

Ethyl selenate Et_2SeO_4 is prepared similarly, d^{25}_4 1.501, n 1.4445.

Methyl and ethyl hydrogen selenates, as well as their lead and potassium salts, are exceedingly unstable substances.

Potassium phenyl selenate $\text{KO} \cdot \text{SeO}_2 \cdot \text{OPh}$ forms colourless leaflets, moderately stable in air, prepared by the action of potassium pyroselenate on a concentrated aqueous solution of potassium phenoxide. Decomposed by hydrochloric acid into phenol and selenic acid (Meyer and Wagner, Ber. 1922, 55, B, 1216).

Production of colourless glass in tank furnaces, with special reference to the use of selenium.—The difference in decolorising power of selenium and sodium selenite is found to be dependent on time, as with more extended melting periods results are more alike. Sodium nitrate did not prevent the liberation of selenium, but produced more intense colours, probably due to the more fusible salt forming a glaze over the other batch materials, which reduced volatilisation of selenium. Borax up to 1 p.c. B_2O_3 had no effect on the coloration. Prolonged heating at the melting temperature (1300° – 1380°) caused intensification of the selenium colour in the case of soda-ash and soda-ash-nitrate melts, but with salt-cake a deepening of the iron-green is noticed, due probably to the very small amount of selenium retained in melts from such batches. Arsenious oxide in the proportion 1.5 per 1000 of sand is most efficacious in preventing the deepening on decolorisation due to selenium. Analysis showed that the proportion of selenium retained in the nitrate batches (up to 40 p.c.) was greater than in any other. In general the amount varied from below 5 p.c. in the salt-cake to 15 p.c. in the soda-ash batches. Apparently selenium did not form selenite in the glass (A. Cousen and W. E. S. Turner, J. Soc. Glass Tech. 1923, 7, 309; J. Soc. Chem. Ind. 1924, 43, B, 218).

Determination of selenium in glass.—Frankel's process (Sprechsaal, 1914, 47, 444) is criticised and the following modification is recommended. Ten grams of finely powdered glass are dissolved in 25 c.c. of hydrofluoric acid and 15 c.c. of water, the dish being cooled to prevent loss of selenium as fluoride. After standing for an hour or so to allow the liberated selenium to coagulate, the mixture is poured into 400 c.c. of boiling water, whereupon the other constituents of the glass dissolve, leaving only selenium, which is collected on a thick paper pad in a Gooch crucible with the aid of the pump. The pad is dropped into a beaker containing 10 c.c. of water, 5 c.c. of hydrochloric acid, and not more than 4 c.c. of very dilute chlorine water (approx. N/60). Gentle warming and agitation of the pad cause complete solution of the selenium. The pulp is filtered off and the filtrate collected in a Nessler tube; 1 c.c. of 5 p.c. gum arabic solution is added, the solution made up to 50 c.c., and 5 c.c. of a 0.5 p.c. solution of phenylhydrazine hydrochloride in water are added. The colour produced is matched against that of similar tubes containing known amounts of selenium. The results are somewhat low. When a commercial glass was tested for selenium in this way, it was found that only 0.00057 p.c. was actually present instead of the 0.0025 p.c. expected, i.e. three-

quarters of the added selenium was lost in the melting (A. Cousen, J. Soc. Glass Tech. 1923, 7, 303; J. Soc. Chem. Ind. 1924, 43, B. 217).

Estimation of selenium.—Dissolution of commercial selenium in nitric acid followed by evaporation to dryness, dissolution of the residue in hydrochloric acid (d 1.175), and precipitation of the selenium by means of sulphur dioxide or a soluble sulphite gave low and very discordant results. Gooch and Pierce's iodometric method (Abstr. 1896, ii. 334) gave somewhat high but concordant results. The most rapid and satisfactory procedure was found to be a modification of Marino's method (Abstr. 1910, ii. 155). A solution in nitric acid is evaporated to dryness and the residue dissolved in dilute sulphuric acid. An aliquot part of the solution is heated to boiling and titrated with 0.2 N-permanganate, adding a slight excess. The precipitated manganese dioxide is filtered off on asbestos, the colour of the filtrate discharged with a measured excess of 0.2 N-oxalic acid, and the titration finished with permanganate (Congdon and Bray, Chem. News, 1924, 128, 266; Chem. Soc. Abstr. 1924, 126, ii. 422).

SEMICARBAZIDE, SEMIOXAMAZIDE, v. HYDRAZINES.

SEMPERVIRINE v. GELSEMINE.

SENARMONTITE. Antimony trioxide, Sb_2O_3 , crystallised in the cubic system. The crystals exhibit optical anomalies and are really pseudo-cubic. They have the form of octahedra up to 2 cm. across, and are sometimes colourless and transparent with a brilliant lustre. Often they are greyish to black, owing to the presence of enclosed needles of stibnite, or red from enclosed kermesite (Sb_2S_2O). Sp.gr. 5.22–5.3; $H.=2-2\frac{1}{2}$. Although less widely distributed than valentinite (orthorhombic Sb_2O_3) and cervantite (Sb_2O_4), yet in Algeria it occurs in much larger quantities. At the Jebel Hamimat mine, 30 kms. S.W. of Ain-Beida, in Constantine, Algeria, it forms stringy veins and nests in calcareous and bituminous shales of Cretaceous age, and has been intermittently mined. At other localities the mineral occurs as an alteration product of stibnite, or at Endellion in Cornwall, of jamesonite. L. J. S.

SENECA OIL. A name given to American petroleum from the circumstance that it was first collected by the Seneca Indians.

SENECIFOLINE AND THE ALKALOIDS OF SENECEO SPP. Of the various species of *Senecio* only three have been examined so far, viz. *Senecio latifolius* (Banks and Soland.) of South Africa, *S. Jacobæa* (Linn.) (ragwort), and *S. vulgaris* (Linn.) (groundsel), which are cosmopolitan in distribution. The two first-named plants are poisonous and cause hepatic cirrhosis in cattle and horses in South Africa, Canada, and New Zealand (Bull. Imp. Inst. 1911, 9, 346).

The toxicity of *S. Jacobæa* seems to vary greatly in different parts of the world.

Senecifoline $C_{18}H_{27}O_8N$ was isolated from *S. latifolius* (Banks and Soland.) by Watt (Chem. Soc. Trans. 1909, 95, 466). It crystallises in colourless, rhombic plates, m.p. 194°–195°, $[\alpha]_D + 28^\circ 8'$ in alcohol, and is soluble in ether or chloroform, insoluble in water or light petroleum. The salts crystallise well and are

lævo-rotatory. On hydrolysis by heating an aqueous solution of the sulphate with alkali the alkaloid furnishes *senecifolinine* $C_8H_{11}O_2N$ (which is very soluble in water and yields a hydrochloride crystallising in rhombic prisms, m.p. 168°, $[\alpha]_D - 12^\circ 36'$) and *senecifolic acid* $C_{10}H_{16}O_6$, m.p. 198°–199°, $[\alpha]_D + 28^\circ 22'$, crystallising in six-sided plates.

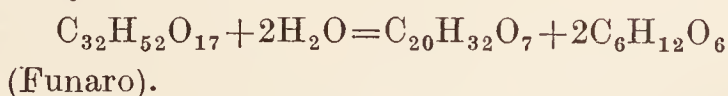
Senecifolidine $C_{18}H_{25}O_7N$ accompanies senecifoline in *S. latifolius* (Banks and Soland.). It forms rhombic plates, m.p. 212°, $[\alpha]_D - 13^\circ 56'$ in alcohol. Salts crystalline.

Senecifoline and senecifolidine are both poisonous; when given in large doses they affect the central nervous system like convulsive poisons, and in smaller doses produce hæmorrhage, which may occur in any organ, but is constant in the liver and is nearly always present in the stomach and bowels. Extracts of *S. vulgaris* produce similar results (Cushny, Proc. Roy. Soc. 1911, B, 84, 188).

Senecionine $C_{18}H_{25}O_6N$ was isolated by Grandval and Lajoux from *Senecio vulgaris* (Linn.) (the common groundsel). It crystallises in rhombic plates, has $[\alpha]_D - 80.49^\circ$ in chloroform, furnishes amorphous salts, and is bitter. It is accompanied by *Senecine*, which yields a sparingly soluble acid tartrate (Compt. rend. 1895, 120, 1120). From Cushny's preliminary observations on *Senecio vulgaris* recorded above, the alkaloids of this plant would appear to resemble senecifoline and senecifolidine in physiological action. G. B.

SENEGA ROOT. *Seneka*, *Snake Root*. *Senegæ Radix*, B. P.; *Senega*, U.S. P. (*Racine de Polygala de Virginie*, Fr.; *Senegawurzel*, Ger.)

The root of *Polygala Senega* (Linn.; Benth. a. Trim. 29), a plant inhabiting the central and northern portions of North America. It is a reputed diuretic and stimulating expectorant, especially applicable to chest diseases and rheumatism. Besides a trace of volatile oil and the constituents common to plants, senega root contains from 2 to 3.5 p.c. of a mixture of saponins, *senegin* and *polygalic acid* (Kobert, Arch. Path. Pharm. 23, 233). Senegin has the formula $C_{32}H_{52}O_{17}$ (?) (Funaro, Gazz. chim. ital. 19, 21). To obtain it the root is exhausted with a mixture of two-thirds alcohol and one-third water, and the liquid, after concentration, is washed by shaking with ether. The syrup thus freed from fixed oil and other substances is precipitated by a mixture of ether (1 part) and alcohol (3 parts), and the crude senegin which falls is finally purified by solution in water, and reprecipitation by ether-alcohol. By the action of dilute acids it breaks up into *sugar* and *senegin*, thus:



The root contains about 5 p.c. of oil. A specimen of the latter had the sp.gr. 0.9616 at 18°; it appeared to contain olein, 73.9 p.c.; palmitin (with a little valerin), 7.9 p.c. (Schroeder, Arch. Pharm. 243, 628). Langbeck (Pharm. Zeit. 1881, 260) first detected methyl salicylate in old specimens of senega, which he supposed to be a product of decomposition of the root. Reuter (Arch. Pharm. [3] 27, 309)

has, however, shown that the *volatile oil* of senega consists of a mixture of methyl salicylate and valerate.

For adulteration of commercial senega root, see Maisch (Pharm. J. [iii.] 20, 547; 21, 46).
G. B.

SENEGAL GUM v. GUMS.

SENEGIN, SENEKA, SNAKE ROOT, v. SENEKA ROOT.

SENGITE. A mining explosive, resembling tonite, sodium nitrate being substituted for barium nitrate; in strength it is nearly equal to gelignite.

SENNA LEAVES. *Sennæ folia*, B. P.; *Senna*, U.S. P. (*Feuilles de Séné*, Fr.; *Sennesblätter*, Ger.) **SENNA PODS.** *Sennæ fructus*, B. P.

This well-known purgative was introduced into European medicine by the Arabian physicians. As it now occurs in commerce, the drug consists of the leaves of *Cassia acutifolia* (Delile) and *Cassia angustifolia* (Vahl). The former species, which some authorities regard as a mere variety of the latter, is found in Nubia and Kordofan, and produces what is known as Alexandrian senna. The latter is cultivated in southern India, and is the source of Indian or Tinnevely senna (*cf.* Benth. a. Trim. 90; Royle, Ill. Bot. Himal. 37).

The latest and most complete chemical investigation of senna is by Tutin (Chem. Soc. Trans. 1913, 103, 2006). A detailed account of the earlier literature is given by Tschirch and Hiepe (Arch. Pharm. 1900, 238, 427). Tutin examined Alexandrian and Tinnevely senna, and senna from Peru botanically identical with the latter variety. In all three samples he identified *aloe-emodin* $C_{15}H_{10}O_5$ (= 'senna emodin' of Tschirch and Hiepe), *rhein* $C_{15}H_8O_6$, and a mixture of *glucosides* of these two substances (=anthraglucosennin of Tschirch and Hiepe). The constitution and properties of the first two substances are given under rhubarb (*q.v.*). Tutin could not find the other substances described by Tschirch and Hiepe; in particular the melting-point of 'senna chrysophanic acid' given by these authors is 25° too low for pure chrysophanic acid.

Of inert substances Tutin identified in all three samples: *myricyl alcohol* $C_{30}H_{62}O$ and 1 : 3 : 4-trihydroxyflavonol (*kaempferol*) $C_{15}H_{10}O_6$. In Tinnevely leaves a new glucoside of this yellow colouring matter was found, *kaempferin* $C_{27}H_{30}O_{16} \cdot 6H_2O$. The other two samples contained also another flavone derivative, *iso-rhamnetin* (Perkin, Chem. Soc. Trans. 1896, 69, 1658), which appears to be identical with 'senna rhamnetin' of Tschirch and Hiepe.

The hydroxymethylanthraquinone derivatives, to which the purgative action of the drug appears to be due, were found by Tschirch and Hiepe to be present in a greater proportion in the fruits than in the leaves; but even in this case the proportion is much less than in *Rheum* or *Frangula*. The Alexandrian leaves were found to contain the largest, and the Tinnevely leaves the smallest proportion of these compounds.

Senna pods appear to contain a greater proportion of cathartic acid than the leaves, and are said to be unattended by the nausea and the pain in the intestines which generally accompany the administration of the leaves (see

Macfarlane (Lancet, 1889, 164) and Salmon (Phar. J. [3] 20, 281)). They were added to the British Pharmacopœia in 1914. G. B.

SENNAAR GUM v. GUMS.

SENSITOL GREEN (Syn. Pinaverdol) v. QUINOLINE.

SENSITOL RED (Syn. Pinacyanol) v. QUINOLINE.

SEPIA. A dark-brown pigment prepared from a black juice secreted by certain glands of the cuttle-fish (*Sepia officinalis*, *Sepia Loligo*, &c.) and ejected by the animal to darken the water when it is pursued. One part of the juice is capable of making 1000 parts of water nearly opaque. The juice, when dried, yields a black mass, which, according to Prout, consists of 78 p.c. black pigment or melanin, 10.40 calcium carbonate, 7.00 magnesium carbonate, 2.16 alkaline sulphates and chlorides, and 0.84 mucus. The black pigment may be isolated by boiling the black mass successively with water, hydrochloric acid, and dilute solution of ammonium carbonate. It is a black, inodorous, and tasteless substance, quite insoluble in water, alcohol, and ether, but remaining suspended in water for a very long time; its deposition may, however, be accelerated by addition of acids or sal-ammoniac. It dissolves in warm caustic potash solution, forming a dark-brown solution, from which it is precipitated by sulphuric and hydrochloric acids, but not by nitric acid. It dissolves also in ammonia, but not in alkaline carbonates.

The pigment is prepared by saturating the dried native sepia with a little caustic lye, then adding more lye, boiling the liquid for half an hour, filtering, precipitating with an acid, washing the precipitate, and drying it at a gentle heat. It is of a dark-brown colour and fine grain.

Os sepia, *Meerscham*, or *White fish-bone*, is the calcareous shell lying within the back of the cuttle-fish. It consists of two layers; the upper thin, but very compact, while the lower is thicker, but porous. The upper layer contains, according to John, 80 p.c. calcium carbonate with traces of phosphate, 9 gelatinous substance, insoluble in water and in cold lime-water, 4 water, and traces of magnesia. The lower layer contains 85 calcium carbonate with traces of potash, 4 gelatinous matter, and 4 water, with traces of magnesia. Forchhammer found in *Os sepia* 0.10 p.c. magnesium carbonate.

Os sepia is used as tooth-powder, for polishing, and for modelling for fine gold articles; it was formerly used as an internal remedy in cases of goitre.

SEPIOLITE v. MEERSCHAUM.

SEPTACROL. An additive product of 3 : 6-diamino-2 : 7 : 10-trimethylacridine nitrate and silver nitrate. A crystalline, hygroscopic powder, soluble in warm water, used as an antiseptic.

SEPTARIA (from *septum*, 'a division'), called anciently *ludus Helmontii* (the *quoits* of Van Helmont, from their form), are argillo-calcareous concretions intersected by veins of calspar, which, when calcined and ground to powder, form an excellent hydraulic cement.

From the regular arrangement of cracks in septaria, which generally assume pentagonal forms resembling in appearance the divisions in the shell of a tortoise, they have received the

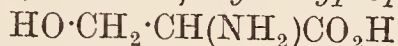
common name of 'turtle stones' or 'fossil tortoises.' The turtle stones found in the Oxford clay at Weymouth, when cut into slabs and polished, form handsome tables. The number of veins of calcspar, upon which their beauty depends, renders these turtle stones unfit for forming an hydraulic cement, in consequence of their furnishing too great a quantity of lime when calcined. Septaria fit for furnishing cement are dredged in Chichester harbour and off the coast of Hampshire, and are also procured from Harwich, Sheppey, and several other places. A stratum of septarian stone, forming the Broad Bench on the coast of Dorsetshire, affords an excellent cement.

SEPTOFORM *v.* SYNTHETIC DRUGS.

SEPTOVINCE. Trichloroacetyl diphenyl dioxide.

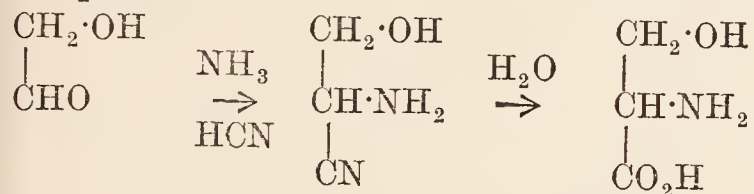
SERICITE *v.* MICA.

SERINE, α -amino- β -hydroxypropionic acid



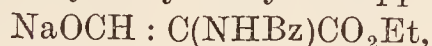
discovered by Cramer (J. pr. Chem. 1865, [i.] 96, 76) among the products of hydrolysis of silk-gelatin; has been similarly prepared from a large number of other proteids. Owing to the difficulty in separating serine the quantity obtained from most of these sources is less than 1 p.c.; silk-gelatin yields 6.6 p.c. (6.81 p.c., Türk, Zeitsch. physiol. Chem. 1920, 111, 69), and salmine 7.8 p.c. Serine occurs free in human perspiration, 1 litre affording 0.09–0.15 gm. of the β -naphthalenesulphonic derivative (Embden and Tachau, Biochem. Zeitsch. 1910, 28, 230).

Synthesis.—Fischer and Leuchs (Sitzungsber. K. Akad. Wiss. Berlin, 1902, 78) effected the first synthesis of serine by the action of ammonia and hydrogen cyanide on glycollic aldehyde, and subsequent hydrolysis of the amino nitrile thus produced—

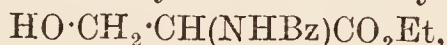


and they showed that on reduction with hydrogen iodide serine gives α -alanine, thus proving the compound to be α -amino- β -hydroxypropionic acid.

A second synthesis is described by Erlenmeyer (Ber. 1902, 35, 3767), and Erlenmeyer and Stoop (Annalen, 1904, 337, 236), in which ethyl sodium hydroxymethylenehippurate



obtained by condensing the ethyl esters of formic and hippuric acids in the presence of sodium ethoxide, is reduced by aluminium-amalgam to the ethyl ester of benzoylserine



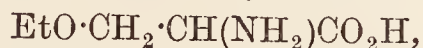
which on hydrolysis yields benzoic acid and serine.

The most convenient method of preparing serine is a third synthetic process due to Leuchs and Geiger (Ber. 1906, 39, 2644), and really a modification of Fischer and Leuch's original method; ethoxyacetal $\text{EtO}\cdot\text{CH}_2\cdot\text{CH}(\text{OEt})_2$, obtained by the action of sodium ethoxide on chloroacetal, yields ethoxyacetaldehyde



on hydrolysis, and this on consecutive treatment

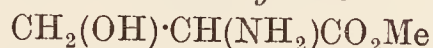
with ammonia, hydrogen cyanide and hydrochloric acid yields β -ethoxy- α -alanine



which on boiling with concentrated hydrobromic acid is converted into serine, the yield being 35–40 p.c. of the theoretical value calculated on the ethoxyacetal used.

dl-Serine. Racemic or inactive serine prepared by any of the above synthetic processes, crystallises in thin colourless leaves, darkens at 225°, melts and decomposes at 246° (corr.); dissolves in 3–4 parts of hot water, or in 23.1 parts at 20°, and has a sweet taste (Fischer and Leuchs, *l.c.*). Treated with nitrous acid serine yields acetaldehyde (Neuberg and Rewald, Biochem. Zeitsch. 1914, 67, 127).

Derivatives.—The methyl ester



is a strongly alkaline syrup forming a crystalline hydrochloride, m.p. 114° (corr.); the *N*-benzoyl ethyl ester $\text{HO}\cdot\text{CH}_2\cdot\text{CH}(\text{NHBz})\text{CO}_2\text{Et}$ forms colourless crystals, m.p. 80°; *N*-benzoyl-*dl*-serine $\text{HO}\cdot\text{CH}_2\cdot\text{CH}(\text{NHBz})\text{CO}_2\text{H}$ has m.p. 171° (Maquenne block); the *dibenzoyl* derivative $\text{BzO}\cdot\text{CH}_2\cdot\text{CH}(\text{NHBz})\text{CO}_2\text{H}$ is sparingly soluble and melts at 124° (Maquenne block); *p*-nitrobenzoyl-*dl*-serine



forms bright yellow thin needles, decomposes at 206°–207° (corr.); β -naphthalenesulphonic-*dl*-serine $\text{HO}\cdot\text{CH}_2\cdot\text{CH}(\text{NH}\cdot\text{SO}_2\cdot\text{C}_{10}\text{H}_7)\text{CO}_2\text{H}$, has m.p. 214° (corr.); *phenyl*-*iso*-cyanate-*dl*-serine $\text{HO}\cdot\text{CH}_2\cdot\text{CH}(\text{NH}\cdot\text{CO}\cdot\text{NHPh})\text{CO}_2\text{H}$ has m.p. 168°–169° (corr.), and yields the *anhydride*, α -hydroxy-methyl- γ -phenylhydantoin, m.p. 168°–169° (corr.). Serine yields a compound, $\text{C}_2\text{H}_{22}\text{O}_{22}\text{NP}_3$, with ethyl metaphosphate (Langheld, Ber. 1911, 44, 2087), and the ethyl ester yields a compound with formaldehyde $\text{C}_9\text{H}_{17}\text{O}_5\text{N}$, b.p. 76°–78°/0.7 mm. (Bergmann, Jacobsen, Schotte, Z. physiol. chem. 1923, 131, 18).

l-Serine. The serine obtained from proteids is the *laevo* isomeride mixed with about 20 p.c. of the racemic compound (Fischer, Ber. 1907, 40, 1501); *l*-serine is obtained by the resolution of *dl*-serine through the fractional crystallisation of the quinine salts of the *p*-nitrobenzoyl derivative; it forms large prisms or six-sided plates, becomes brown at 211° (corr.), and decomposes at 228° (corr.), it is more readily soluble than the racemic compound, and has a sweet taste; it has $[\alpha]_D^{20}$ –6.83° in aqueous, or +14.45° in normal hydrochloric acid solution (Fischer and Jacobs, Ber. 1906, 39, 2942).

Aminoethyl alcohol was isolated from the products of the decomposition of serine by putrefactive bacteria. Ten grams of the amino-acid yielded 2.8 grams of crude aminoethyl alcohol picrolonate (Nord, Biochem. Zeitsch. 1919, 95, 281).

Derivatives.—The methyl ester



is a thick alkaline syrup, readily passes over into the *anhydride*, and forms a crystalline hydrochloride that decomposes at 167° (corr.); the *p*-nitrobenzoyl derivative



dissolves in 180 parts of water at 25°, and has

$[\alpha]_D^{20} + 43.56^\circ$. *l*-Serineanhydride $C_6H_{10}O_4N_2$ decomposes at 247° (corr.) and has $[\alpha]_D^{20} - 67.46^\circ$ (Fischer and Jacobs, *l.c.*).

l-Serine is converted into *d*-alanine by the following series of reactions: methyl-*l*- β -chloro- α -aminopropionate, m.p. 157° (decomp.), obtained by the action of acetyl chloride and phosphorus pentachloride on the hydrochloride of *l*-serine methyl ester, yields on hydrolysis *l*- β -chloro- α -aminopropionic acid, which is reduced to *d*-alanine by sodium amalgam (Fischer and Raske, Ber. 1907, 40, 3717). The conversion of *l*-serine into *l*-cystine is effected by treating the hydrochloride of *l*- β -chloro- α -aminopropionic acid with barium hydrosulphide and oxidising the product with atmospheric oxygen in the presence of ammonia (Fischer and Raske, Ber. 1908, 41, 893).

d-Serine is obtained by resolution of *dl*-nitrobenzoylserine through the quinine salt and subsequent hydrolysis; it can be prepared also in good yield by allowing yeast to grow in a solution of racemic serine containing a large excess of sucrose, both isomerides are attacked by the yeast, but the *l*ævo is destroyed far more rapidly than the *d*extro variety (Ehrlich, Zeit. Ver. deut. Zuckerind. 1906, 608, 840; Biochem. Zeitsch. 1908, 8, 464). In crystalline form, melting-point, and solubility *d*-serine is the same as *l*-serine, it has, however, a much sweeter taste, and has $[\alpha]_D^{20} + 6.87^\circ$ in aqueous, or -14.32° in normal hydrochloric acid solution (Fischer and Jacobs, *l.c.*).

Derivatives.—The copper salt forms deep blue prisms insoluble in alcohol; the *p*-nitrobenzoyl derivative $HO \cdot CH_2 \cdot CH(NH \cdot CO \cdot C_6H_4 \cdot NO_2)CO_2H$ has m.p. 189.5° (corr.) with decomposition, is more readily soluble than the racemic compound, and has $[\alpha]_D^{20} - 43.74^\circ$ (Fischer and Jacobs, *l.c.*).

*iso*Serine, β -amino- α -hydroxypropionic acid $H_2N \cdot CH_2 \cdot CH(OH)CO_2H$ is not found naturally, nor does it occur among the products of hydrolysis of proteids. M. A. W.

SEROTIN *v.* GLUCOSIDES.

SERPENTARY RHIZOME. The dried rhizome and roots of *Aristolochia serpentaria* (Linn.) and *A. reticulata* (Nutt.).

SERPENTINE. A rock much used as a decorative stone, and often popularly called a 'marble.' It has about the same hardness and density as ordinary marble, but is usually tougher and does not possess a crystalline texture. Essentially, it is a hydrous magnesium silicate, with more or less iron. Since this massive serpentine-rock consists mainly of a single mineral species, the name serpentine is also applied to the pure mineral. This is a hydrated magnesium silicate $H_4Mg_3Si_2O_9$, in which a small proportion of the magnesia is often replaced by an equivalent amount of ferrous oxide. It never occurs distinctly crystallised. Sp.gr. 2.5–2.65; H.=2½–4, rarely 5.5. It is decomposed by hydrochloric and sulphuric acids; and before the blowpipe fuses on the edges with difficulty.

Serpentine, as a rock, usually exhibits dark shades of green and red, variously clouded and blotched, like the skin of a serpent, whence its name, as also the term *ophite* (ὄφις, a serpent),

by which it is sometimes known. The rock may be veined with steatite, or rendered more or less porphyritic by enclosed crystals of bastite or bronzite, or may contain garnets, usually altered to kelyphite or chlorite, as may be well seen in the pyrope-bearing serpentine of Zöblitz, in Saxony. The beauty and variety of its colours have led to the extensive use of serpentine for vases and other ornamental objects. It is also employed for mantel-pieces and architectural columns, but the rock is usually so broken up by joints that it is difficult to procure slabs of large size. While valuable for indoor decoration, it is apt to yield on exposure to the atmosphere, gradually losing lustre and presenting an eroded surface. From its refractory behaviour on exposure to heat, it is sometimes employed in the construction of ovens. It has also been used as a source of certain magnesium salts, such as the sulphate.

Serpentine has been extensively worked in the Lizard district in Cornwall, but not elsewhere in Britain, though it occurs in Anglesea, Ayrshire, and Banffshire. On the Continent, serpentine has been worked for centuries at Zöblitz and elsewhere in Saxony. It is also wrought in the Vosges and in the departments of the Hautes Alpes, Lot, and Aveyron in France; while in Italy the most famous locality is at Prato in Tuscany, which yields a dark-green variety known as *verde di Prato*, resembling when polished an antique bronze, and hence largely used for statues, &c.

The following analyses of the different varieties of serpentine from the Lizard district are quoted from J. J. H. Teall's British Petrography, 1888, 124, where an excellent account of British serpentines is given. (For analyses of Scotch serpentines, see M. F. Heddle, Mineralogy of Scotland, 1901, 2, 130.) I, Black, with porphyritic crystals of bastite, from near Cadgwith (also FeS_2 0.41). II, Greyish-green, granular, from Porthalla. III, Dark oil-green, from Porthalla. IV, Reddish-brown, granular, from Porthalla. V, Ornamental serpentine from the Lizard (also Cr_2O_3 0.08):—

	I.	II.	III.	IV.	V.
SiO ₂ . .	38.50	38.60	37.15	39.50	38.86
Al ₂ O ₃ . .	1.02	0.10	5.60	5.08	2.95
Fe ₂ O ₃ . .	4.66	11.55	1.10	8.12	1.86
FeO . .	3.31		8.80		5.04
NiO . .	0.59	—	—	—	0.28
CaO . .	1.97	trace	0.10	trace	trace
MgO . .	36.40	33.62	32.80	34.65	34.61
Alkalis, &c.	—	3.31	0.29	0.10	1.10
H ₂ O . .	12.35	12.82	14.16	12.55	15.52
	100.58	100.00	100.00	100.00	100.30
Sp.gr. .	2.59	2.65	2.56	2.54	2.59

Pseudomorphs of serpentine after large crystals of olivine occur at Snarum in Norway, and retain in some cases a nucleus of the original mineral. Most serpentines have, in fact, been derived from peridotites (*q.v.*), or rocks rich in olivine; though other minerals, such as hornblendes and pyroxenes, may also be converted into serpentine.

Several mineral varieties of serpentine have received distinctive names. *Noble* or *precious serpentine* is a fine translucent variety of oil-green or yellowish-green tint; this is worked at Iona in the Hebrides, and Snarum in Norway. *Picrolite* is the term

applied to the mineral when presenting a columnar or fibrous structure, while an asbestiform variety with silky fibres is known as *chrysotile*. Much of the mineral used in the arts under the name of asbestos (*q.v.*) or amianthus occurs in veins running through massive serpentine, especially in Canada, and is really chrysotile. Serpentine with a lamellar structure is termed *marmolite*, and a shaly variety of dark-green colour from the Antigorio valley in Piedmont is known as *antigorite*. *Williamsite* is a translucent apple-green serpentine, found in limited quantity at a chromite mine at Texas in Pennsylvania, and is cut as an ornamental stone. An exceptionally hard serpentine, termed *bowenite*, has been mistaken for jade, and C. A. McMahon has shown that the so-called jade of Afghanistan is of this character (Min. Mag. 1890, 9, 187).

Serpentine frequently carries chrome iron-ore; and crystals of chromite and picotite are common microscopic enclosures in the rock. Native copper also occurs in serpentine, and large masses upwards of a ton in weight were obtained many years ago from fissures in serpentine at the Trenance mine, near Mullion, in Cornwall. Nickel ores and platinum also occur in association with serpentine-rocks.

It is not uncommon for serpentine to be intimately associated with limestone or dolomite, forming a rock known as *ophicalcite*, *ophiolite*, or *serpentinous marble*. The composite rock, being variegated with green and white colours, is prized as an ornamental material, but on exposure to atmospheric influences a differential action is set up, and the surface becomes unequally eroded. The famous *Verd antique* is a brecciated ophiolite (*v. MARBLE*).

References.—J. Watson, *British and Foreign Marbles and other Ornamental Stones*, Cambridge, 1916. For American serpentines *v. G. P. Merrill*, *Stones for Building and Decoration*, 3rd ed., New York, 1903. L. J. S.

SERPENTINE-ASBESTOS *v. ASBESTOS*.

SERVICE BERRY. The seeds of the service berry (*Sorbus aucuparia*) contain about 22 p.c. of a yellow oil, sweet tasting, mobile, which rapidly dries on exposure to air, sp.gr. 0.9317 at 15°; refract. index at 15°, 1.4753; acid value 2.35; sapon. value, 208.0; iodine value, 128.5; iodine value of the fatty acids, 137.5; acid value of the fatty acids, 230.2 (van Itallie and Nieuwland, Arch. Pharm. 1906, 244, 164; J. Soc. Chem. Ind. 1906, 595).

SESAMÉ OIL (*Beniseed Oil*, *Gingelli Oil*, *Teel Oil*). Sesamé oil is obtained from the seeds of the sesamé plant, *Sesamum indicum* (Linn.), belonging to the family of *Bignoniaceæ*. The original home of *Sesamum indicum* is unknown. According to A. de Candolle, sesamé seed was brought from the Sunda Islands to India several thousand years ago, and has migrated thence through the Euphrates basin to Egypt.

India produces the largest amount of varieties; there the white seed, yielding the best Indian oil, is termed *suffettil*, whilst the black variety, containing the largest proportion of oil, is known as *tillie*. In the trade a mixture of white and dark seeds bears the name 'bigarré.'

According to the rules of the trade, white sesamé must contain at least 85 p.c. of white

seeds. If the proportion of dark seed exceeds 15 p.c., an allowance is made. If the dark seed exceeds 25 p.c., the term white sesamé seeds no longer applies.

The bigarré quality must contain at least 35 p.c. of white seeds. The commercial seed known as 'grosses graines' must not contain more than 20 p.c. of 'petites graines.' No more than a maximum of 50 p.c. of small seeds is permitted; if they make up from 20 p.c. to 50 p.c., an allowance must be made.

By far the largest quantity of *Sesamum indicum* is grown in East India (the 1909-1910 crop amounted to 516,000 tons), Java, Siam, Tonkin, China, and Japan. Large quantities are also grown in the countries bordering the Mediterranean, especially in the Levant and Egypt. The seed grown in Africa belongs to the species *Sesamum radiatum*, Shum and Thonn.

Smaller quantities are produced in Algeria and on the West Coast of Africa, as also on the East Coast (Mozambique, Zanzibar, East Africa). In Southern Rhodesia the seed is cultivated by the natives; it is not unlikely that in the near future it may be exported to Europe.

In South America, the plants are grown in Brazil and Venezuela, Mexico, the southern states of America, and in several islands in the West Indies. The chief emporium for the importation of sesamé seed into Europe is Marseilles, where all grades of sesamé oil from the Levant, the Indies, and West Africa are crushed.

Since the admixture of sesamé oil to margarine has become obligatory in Germany, Austria, and Belgium, a considerable sesamé oil industry has rapidly sprung up in those countries. The quantities consumed by these countries, prior to the war, were in the inverse order, viz. Belgium, Austria, and Germany.

The sesamé oil industry has not been able to obtain a foothold in Great Britain, inasmuch as the finer qualities of sesamé oil, which are obtained in the first expression, do not find so remunerative an outlet as they do in other countries; in fact, the whole of the oil would have to be disposed of as soap oil. The small amount of seed imported into this country is used in the manufacture of compound cake (*see OILS, FIXED, AND FATS*), the high proportion of oil in sesamé seed helping to bring up the percentage of oil in the mixed meal to the legally prescribed amount. The proportion of oil in sesamé seeds varies from 50 to 57 p.c.; hence the seed must be subjected to repeated expressions in order to yield the full amount of oil. The practical yields from sesamé seeds of different origin vary from 42 to 48 p.c.

The oils of the first expression in the cold represent the best qualities. The finest edible sesamé oil is obtained from the Levant seeds. Of these, the best brands are harvested in the Jaffa district. Slightly inferior in flavour to the Jaffa oil are the products obtained from seed grown in Caiffa, St. Jean d'Acre, Tarsus, Smyrna, Mersyna. The oil from Alexandretta seeds represents a lower grade still. The Indian seeds, embracing chiefly those from Kurrachee and Bombay, give oils of more unpleasant flavour, and are therefore not usable

for the best kinds of margarine. Lower still, as regards taste and flavour, rank the oils from Chinese and African seeds. In China the seeds are roasted before being ground and expressed in wedge presses. Owing to this process the oil becomes dark-coloured and acquires a strong flavour of nuts. The largest quantities of Chinese sesamé oil were used in the German margarine industry.

The oils of second and third expression are used for manufacturing purposes, chiefly for soap-making. The average composition of sesamé cake is the following:—

	Per cent.
Oil	14·63
Moisture	7·65
Proteins	36·14
Ash	13·17
Crude fibre	4·83
Carbohydrates	23·58

When the seed does not arrive in a sound state, the oil is extracted with solvents for the complete recovery of the oil, and the extracted meal is sold as manure.

For the chemical and physical characteristics of sesamé oil, *see* OILS, FIXED, AND FATS.

Sesamé oil contains from 12 to 14 p.c. of solid acids, the remainder consisting of oleic and linolic acids. Sesamé oil is dextro-rotatory, a property which may supply a useful additional means of identifying the oil. The optical activity is no doubt due to the presence of phytosterol and sesamin which form the bulk of the unsaponifiable matter in sesamé oil. In addition thereto, there occurs in the unsaponifiable matter a thick non-crystallisable oil, sesamol, which gives the characteristic colour reaction known as the 'Baudouin test' (*see* OILS, FIXED, AND FATS).

The Baudouin colour reaction for sesamé oil is greatly weakened in intensity and may be completely destroyed for dilutions of 40 p.c. and under by heating the oil at 250°C. for $\frac{1}{2}$ hour in the air, or at 120°C. for 24 hours *in vacuó*. It is also weakened by treatment of the oil with absorbents such as animal charcoal. For this reason the absence of a positive Baudouin reaction cannot be taken as proof of the absence of sesamé oil, particularly in the case of margarines, which may only contain a small proportion of highly refined oil (H. Heller, *Farben-Zeit.* 1923, 28, 1528–1529; *J. Soc. Chem. Ind.* 1923, 42, 896, A).

According to G. O. Gravenhorst (*J. Ind. Eng. Chem.* 1924, 16, 47), the coloration given by genuine sesamé oil in the Baudouin test depends, to some extent, on the origin of the oil; the intensity of the coloration is affected considerably by a decrease in the strength of the hydrochloric acid used, the strongest reaction being obtained with an acid of sp.gr. 1·190 to 1·197. The presence of a moderate amount of free chlorine in the acid is without influence on the test. Whilst rancid sesamé oil will give a normal reaction with the test, a mixture of sesamé oil with arachis oil or butter ceases to give a coloration when it has become badly rancid. If, however, the rancid mixture is washed with warm 5 p.c. sodium hydroxide solution and then dried, it will yield a normal coloration when subjected to the test (*Analyst*, 1924, 49, 142).

The cold-drawn sesamé oil is largely used as an edible oil, notably so, as pointed out above, in the manufacture of margarine. Since small quantities of sesamé oil are easily revealed by the Baudouin test, it was, until a few years ago, obligatory in Germany and Austria to use at least ten parts of sesamé oil in the manufacture of margarine for 100 parts of fatty matters, but the regulations were subsequently modified, so that it was unnecessary to add any specified quantity of the oil provided that the margarine gave a distinct reaction in the test. In Belgium, 5 p.c. were prescribed. The best oils are consumed as table oils; small quantities of this class are used in the production of perfumes ('*enfleurage*').

Sesamé oil is used to a considerable extent as an adulterant of olive oil. Villavecchia's test for its detection in olive oil sometimes fails, because in the process of pressing the olives an aqueous liquid containing a colouring matter, soluble in the oil, is collected along with the oil, which reacts with Villavecchia's reagent to produce a rose colour. By heating the oil with a 10 p.c. solution of ammonia in alcohol it no longer gives the rose tint with the hydrochloric acid furfural reagent (*Prax*, *Ann. falsific.* April–May, 1922).

The best cold-drawn oil being rather high in price, adulteration of the best qualities with poppy seed oil, cotton seed oil, and arachis oil is not infrequent. The sesamé oils of second and third expression are adulterated with rape oil.

The lower qualities of sesamé oil find a large outlet for soap-making in the south of Europe; they are also used as burning oil and for making india-rubber substitutes. The oil expressed from Chinese yellow sesamé seeds has been examined by well-known methods. The saturated and unsaturated acids were separated, and the former were methylated and separated by fractional distillation under reduced pressure, and the usual constants determined on the fractions, from which the fatty acids were subsequently liberated and crystallised. The unsaturated acids yielded no hexabromide, but linolic tetrabromide separated, and calculation from the iodine value showed the presence of oleic acid. The percentage composition of the glycerides is calculated to be as follows: oleic, 48·1; linolic, 36·8; palmitic, 7·7; stearic, 4·6; arachidic, 4; lignoceric acid, trace; and unsaponifiable matter (G. S. Jamieson and W. F. Baughman, *J. Amer. Chem. Soc.* 1924, 46, 775; *Analyst*, 1924, 49, 236). J. L.

SEWAGE. The problem of sewage purification has been gradually forced on the country owing to the evils arising from the pollution of the streams, and to the increased flow of sewage resulting from the general introduction into our towns of the water-closet system, viz. water-borne sewage. Another source of pollution, although less serious than that of sewage, is manufacturing refuse.

Sewage may be defined as the water supply of a town after it has been used. It contains the solid and liquid excreta of the population, household drainage, containing a great variety of animal and vegetable remains derived from the food, the bathing, and the washing of the household.

With the exception of a few towns sewered

on a dual system of drainage, sewage also contains the washings of the street, and storm water, and in any large community trade waste of a complex character forms a part of it.

The separate system of drainage is only sanctioned by the Ministry of Health in cases where surface water can be discharged by separate drains without creating a nuisance, and where the combined system would be unduly costly.

Water-borne sewage never has the same composition in any two cities, and in any given sewer the character of the sewage varies with the hour of the day, the season of the year and the state of the weather.

The creation of Rivers Boards in 1891, and subsequently of River Authorities to enforce the provisions of the Rivers Pollution Prevention Act, 1876, directed inquiry into the practical efficiency of the systems of sewage disposal in operation in works of sanitary authorities, and revealed the great difficulties experienced by these bodies in devising means and maintaining works for the efficient purification of the sewage of their districts. Especially has this been so in the case of the County and non-County Boroughs in England, and it has been found necessary to insist on more efficient means being adopted for the effectual purification of the sewage by these authorities.

The first and necessary step to take in the purification of sewage is to remove as much of the matters in suspension as is economically possible. On arriving at the outfall works the sewage is usually passed through coarse screens of various design. In large works, automatic appliances are provided. Then the sewage is passed through detritus tanks designed so that the speed of flow will allow the heavier and mineral matters to settle out of the sewage, leaving the lighter mineral and organic suspended matters to pass forward with the sewage to tanks for further treatment. Tank treatment may have for its object:—

(a) The removal of the remaining suspended matters in the sewage by quiescent sedimentation or continuous flow sedimentation (sedimentation tanks).

(b) Sedimentation with partial digestion of the insoluble and soluble organic matters (septic tanks); or

(c) Sedimentation aided by the use of various chemicals causing a flocculent precipitation and more rapid settlement of suspended matters (precipitation tanks).

The choice of tank treatment depends upon a number of factors affecting the particular sewage under treatment. The quality of the sewage, the time required to effect a maximum reduction of the suspended solids, and the economical concentration of the sludge produced have to be considered having regard to the final treatment of the sewage by filtration. Some sewages contain more solids which settle very slowly than other kinds, and no precise rules can be laid down as to the design of the tanks or as to the period of settlement required; but with regard to the holding capacity of the tanks, the minimum requirements for sedimentation, septic, and chemical precipitation tanks are fixed by the Ministry of Health Regulations (*see pp. 75 et seq.*).

The 'septic tank treatment' of sewage has not fulfilled the claims that were put forward on its introduction as to the advantages of the treatment. It was primarily claimed that it solved the sludge difficulty, inasmuch as practically all the organic solid matter was digested in the tank. Experience has shown, however, that only a small percentage of the organic solids are digested, the amount varying to some extent with the character of the sewage, the size of the tanks relative to the volume treated, and the frequency of cleansing. It was also said that sewage which had passed through a septic tank was more easily oxidised than sewage from which the solids had been allowed to settle, either with or without the aid of chemicals, in tanks which were frequently cleaned out; but here again experience has shown that septic tank effluent is not more easily oxidised than the other liquids. The septic tank does not effectively remove the suspended solids in the sewage, the tank liquid containing on an average from 10 to 15 grs. of suspended solids per gallon—an amount that materially affects the maintenance of the filters used for the final purification. Moreover, a slow rate of flow through the tanks tends to increase the risk of nuisance from smell, when the septic effluent is distributed over a filtering area. The sewage ought not to remain more than 24 or less than 12 hours in a septic tank. The longer the tank is run without cleaning the less *volume* of sludge there will be per given volume of sewage treated, but the amount of suspended solids issuing from the tank increases seriously as time goes on and greatly affects the efficient working of the filters and the quality of the filtrate. On the other hand, the main use of a septic tank, owing to its large capacity, is, that it has the effect of equalising the sewage as regards strength, and of keeping the character of the liquid uniform, and the Royal Commission (5th Report) think that in certain circumstances the adoption of septic tank treatment as a preliminary process is efficient and economical.

If there be any advantage in attempting to ferment the organic solids of sewage, it would appear preferable to avoid the disturbance of the sludge in the bottom of the tank through the evolution of gas by separation of the sludge from the flowing sewage and to submit the sludge to septic treatment in a special chamber provided for the purpose. This principle has been carried out to some extent by Travis, who has devised a hydrolytic tank and installed the process at Hampton. The tank is so designed that only a small proportion of the sewage comes in contact with the sludge, but difficulties in preventing nuisance and the efficient removal of the suspended matter have prevented its general adoption. In the septic tank designed by Imhoff, and known as the Essen tank, the flowing liquid is entirely separated from the sludge. The tank is of cylindrical form with a conical bottom. In the upper portion of the tank is a sedimentation chamber with sloping floors and slots at the bottom to allow the sludge to settle into the sludge chamber below (Surveyor and Municipal and County Engineer, 1909, 625). It is claimed that the sludge which is withdrawn from this chamber from time to time contains only 75 p.c. water and is non-

putrefactive, and that a large percentage of the organic solid matter is destroyed. The method has been adopted by the Emscher Genossenschaft, but only a limited number of installations have been put down in this country. The Imhoff tank at Manchester is an efficient clarifier. Drying beds handle the digested sludge satisfactorily.

With regard to the chemical precipitation of sewage, it has long been known that no amount of chemicals which can with any show of reason be added to sewage is sufficient, or nearly sufficient, to convert the whole of the putrescible matter into harmless forms. All methods of chemical treatment of sewage, by patented processes or otherwise, aim at clarification and purification; that is, the separation of the solids and the clarification of the liquid, usually by chemical precipitants. Mere precipitation processes cannot, however, be relied upon to remove sufficient of the soluble putrescible organic matter to prevent the effluent subsequently becoming offensive to the senses. The treatment of the sewage by chemical precipitation, whilst effecting considerable purification, at the same time brings the effluent into a condition more suitable for subsequent filtration, especially where the deposition tanks are small for the volume of sewage to be treated. Hence the use of chemicals can only be recommended for the purpose of starting a process of purification, and the only practicable way of purifying the soluble putrescible organic matters of the liquid sewage resulting from the precipitation process is to resort to filtration. That filtration in some form or another is essential to any efficient system of sewage purification has been established over and over again, and insisted upon by high authority. It is therefore important that we should understand the scientific principles involved in the process of filtration which are available for the purpose. We must first define what is, or ought to be, the true aim of sewage purification. It is to remove the suspended matters, and to convert the carbon and the nitrogen of the remaining organic matter in the sewage into inorganic matter. The River Pollution Commissioners in 1868, with this aim in view, advocated filtration through land. They laid down conditions essential for successful results which are as true to-day as they were at that date, although subsequent researches have thrown new light on the true causes of the conversion of the organic matter into inorganic matter and assisted materially to a more satisfactory solution of the problem. They found that in filtration, whether through sand, gravel, chalk or soil, or through a mixture of chalk and sand, it was essential that atmospheric oxygen should have frequent and free access to the interior of the filter, and that the effluent should flow freely off from the bottom of the filter, so that as the last portion of each dose of sewage water sinks into the filter it may draw atmospheric air into the pores of the material from the surface downwards. They regarded the action as a mechanical and chemical one, and showed that the action could be maintained if the oxidising powers of the filtering material were not allowed to become choked. The subsequent researches of Schloesing and Muntz in France (*Compt. rend.* 1884, 301; 80, 1250) and of Robert Warington in England

(*Chem. Soc. Trans.* 1877) have shown that purification as defined above is brought about by the intervention of living organisms. Sewage contains various kinds of organic matter which furnish abundant food for bacteria, which are always present in great numbers.

The changes brought about in the condition of sewage on standing may be of a twofold character. The one, due to living organisms requiring free oxygen for their growth, has the result of rendering the organic matter inoffensive. The other, due to organisms which flourish in the absence of free oxygen, gives rise to products which are offensive. The oxygen necessary for the growth of what may be termed the aerobic organisms is usually derived from the oxygen dissolved in the water which carries the sewage; but sewage itself is either entirely free from, or at any rate contains less dissolved oxygen than is necessary for the active growth of these aerobic organisms. In consequence of the absence of dissolved oxygen in sewage, it has during its passage to the outfall works already begun to undergo change of a putrescent character owing to the growth of the putrefactive or anaerobic organisms. The products of this putrefactive change rapidly absorb free oxygen passing into more stable forms, and therefore when sewage is poured into a river or into fresh water it rapidly robs the water of its dissolved oxygen, and if the quantity poured in exceeds a certain proportion as compared with the river or fresh water, the whole of the water is deprived of its dissolved oxygen and becomes incapable of supporting the activity of the aerobic organisms, whilst at the same time the activity of the putrefactive or anaerobic organisms may render the whole of the waters noxious.

The kind of decomposition which sewage undergoes is therefore determined by the kind of microbes which can freely develop and remain active in sewage, and the kind of microbes which can develop and remain active is, in turn, determined by the access or exclusion of air and light, by temperature, and by the chemical reaction of the whole. These facts are of prime importance, for they furnish the basis of all good systems of sewage disposal. The prompt disposal of sewage is the end and aim of any rational system of sewage disposal. Putrefactive processes are slow and often a menace to the health of a neighbourhood.

Processes of oxidation are more rapid and complete and are inoffensive. Warington showed that, under favourable conditions, these living organisms in sewage may be so cultivated as to effect the destruction of the organic matter, provided the filter is well supplied with the air requisite for the discharge of the functions of these organisms, and also that sufficient mineral matter of a suitable kind be present to combine with the products of their action. The results of the experiments made by the American chemists (1891) of the Massachusetts Board of Health, confirm this statement, for they say:—

‘The purification of sewage by intermittent filtration depends upon oxygen and time; all other conditions are secondary. Temperature has only a minor influence; the organisms necessary for purification are sure to establish themselves in a filter before it has long been in

use. Imperfect purification for any considerable period can invariably be traced either to a lack of oxygen in the pores of the filter or to the sewage passing so quickly through that there is not sufficient time for the oxidation processes to take place. Any treatment which keeps all particles of sewage distributed over the surface of sand particles, in contact with an excess of air for a sufficient time, is sure to give a well-oxidised effluent, and the power of any material to purify sewage depends almost entirely upon its ability to hold the sewage in contact with air. It must hold both sewage and air in sufficient amounts. Both of these qualities depend upon the physical characteristics of the material. The ability of a sand to purify sewage, and also the treatment required for the best results, bear a very close relation to its mechanical composition.

Plants built to answer the above conditions consist of a number of sand beds, each of about one acre superficial area and from 4 to 5 ft. in depth, carefully levelled, underdrained and divided from each other. Crude sewage, after passing through a grit chamber and screens to remove road washings and large floating substances, is run successively upon the various beds, none of the beds receiving sewage for a longer period than 6 hours out of each 24, for if the beds received the sewage continuously there would be absolutely no air present at any time in the bed, and air is necessary for the life of the aerobic organisms. By applying the sewage only 6 hours out of the 24, as the liquid drains out of the bed, air enters to take its place, and the conditions favourable to the action of both groups of organisms are maintained. By this process from 50,000 to 75,000 gallons of domestic sewage, sewage not containing a large proportion of manufacturing waste, can be purified each day on one acre of sand-bed area, so that the polluting substances are to such an extent removed that the liquid, as it runs away from the bed, is clear, bright, almost odourless, and can be emptied into a very small stream without fear of causing trouble (L. P. Kinnicutt).

Decomposed sludge from septic tanks contains methane bacteria, and considerable quantities of gas containing methane, carbon dioxide, and nitrogen may be obtained from it. It can also be used to ferment calcium acetate, whereby calcium carbonate, methane, and carbon monoxide are obtained. Hydrogen is never obtained by the further decomposition of the sludge, and its occurrence must be ascribed to the presence of more recent sludge. By repeated decantation of the decomposed sludge, mixed with nutrient inorganic material and with calcium acetate solution, a preparation is obtained which sets up methane fermentation more quickly and energetically than the untreated sludge. The presence of nitrogen in the gas from sludge fermented in presence of calcium acetate is due to the breakdown of organic nitrogen compounds and not to the denitrification of nitrites, and the undiminished nitrogen content in gas from sludge which has been repeatedly fermented must be ascribed to the decomposition of dead bacteria. The presence of nitrites may inhibit, partially or completely, the methane fermentation. The

concentration of the bacteria has a marked influence on the rate of fermentation, and a certain minimum of decomposed sludge is necessary for its continuance (Bach and Sierp, *Zentr. Baktr. u. Parasitenk.*, 1923, ii. Abt. 60, 318; *Chem. Zentr.* 1924, 95, 1, 369; *J. Soc. Chem. Ind.* 1924, 43, B. 275).

The application of sewage to land is carried out by two processes, which are known as intermittent downward filtration and broad irrigation. In the former, the land is used after the manner of an ordinary sand filter and requires the land to be open and porous with a sandy subsoil. With land of a retentive character, with a clay subsoil, broad irrigation is usually adopted, the sewage being distributed over the land in such a manner that it runs over the surface, and the purification is effected by the nitrifying organisms in the surface soil. As some irrigation areas, are, however, underdrained in order to assist the land to 'dry off' sufficiently rapidly, a certain amount of downward filtration may take place, and it is therefore difficult to make a distinction between the two processes in every case. In both intermittent downward filtration and broad irrigation it is desirable to intercept some of the suspended solids in the sewage before applying the liquid to the land. In sewage farming proper, the preliminary treatment is very slight and usually consists of straining and rough settlement.

The volume of sewage that can effectively be purified on a given area of land varies within wide limits, depending on the quality of the land and the strength of the sewage. The general experience is that on good land a sewage of average strength from which the major portion of the suspended solids has been eliminated by tank treatment can be treated at about the rate of 30,000 gallons per acre per day, with the production of a high-class effluent. With unsuitable land, such as clay, not more than 3000 gallons per acre can be efficiently treated, even after settlement of the sewage.

The Ministry of Health requires, when the sewage after previous sedimentation is applied to land of the most suitable kind by broad irrigation, that the quantity should not exceed 4500 gallons of dry weather flow per acre per day, or the dry weather flow sewage from 150 persons. Surplus land must also be provided in such cases from 25 p.c. to 50 p.c. for resting purposes. When the land is less suitable the quantity per acre may be reduced to as little as 1000 gallons per day. When the sewage, after previous sedimentation, is applied to downward filtration on land, the quantity per acre of the most suitable land shall not exceed 15,000 gallons of dry weather flow per acre per day, or the sewage from 500 persons. Surplus land up to 25 p.c. is usually required. This area to be increased if the land be not of the best. When the sewage, after chemical precipitation, is applied to land, the tank effluent may be applied at the rate of 30,000 gallons per acre per day, or the sewage from 1000 persons as a maximum.

Land naturally varies in its physical character and in its power to purify sewage. Moreover, climatic conditions play an important part, and although the volume of sewage which land is

capable of dealing with is sufficient to warrant the smaller sanitary authorities in adopting land filtration, and it is the cheapest of all systems in such cases, yet it has been successfully contended that in many cases, especially in the great centres of manufacturing industry, the land available is either of unsuitable quality, is available in quite inadequate area for effective filtration through the soil, or is obtainable only at a prohibitive cost, and it is now recognised that sewage purification may, in such cases, be carried out on comparatively small areas artificially prepared.

Artificial sewage filters may be divided into two broad classes: contact beds and percolating filters.

Contact-bed treatment.—This method is the result of experiments made by W. J. Dibden, on London sewage. It differs from intermittent downward filtration in that the sewage instead of being applied slowly and allowed to drain through the land, is run rapidly into a watertight bed, filled with a coarse material as cinders, clinkers, or coke, and retained in the bed for a given number of hours, after which the liquid is quickly run out of the bed. The bed, after it is emptied, is allowed to remain empty for some time before receiving the next filling. The beds are usually built on two levels so that if sufficient purification is not accomplished by single contact, the liquid from that bed can be run upon a second bed at a lower level and receive double contact.

The method is not adapted for treating crude sewage or sewages containing much suspended matter, and the capacity of a contact bed is best maintained by preventing, as far as possible, the access of suspended and colloidal matters to the bed.

The physical, chemical, and bacterial changes which take place during the process of purification in a contact bed are complicated. The formation of colloidal film deposits on the surface of the filtering medium, and the action of micro-organisms is essential to the process. In order to regulate the growth of this slimy deposit so that the bed will do its proper work, and at the same time not lose its liquid capacity, it is essential to carefully regulate the cycle of operations, especially providing a period of rest for the bed to remain empty before refilling, as the resting period is the most important phase of the cycle, when oxidation is most active. A bed should not be filled more than three times in 24 hours, and the fillings should be as far apart from one another as practicable, viz. three fillings in three cycles of 8 hours each, so that the maximum period for drainage and aeration between the fillings may be obtained.

The depth of contact beds should not exceed 6 ft. or be less than 2 ft. 6 ins. In deciding upon the size of the material to be used, the amount of suspended matter in the liquid to be treated must be considered. As a general rule, the greater the amount of suspended matter in the liquid the larger the material should be. Material of a diameter from $\frac{3}{8}$ to $\frac{5}{8}$ of an inch down to as fine as $\frac{1}{4}$ inch diameter may be used. Over the drains of the beds, material of fairly large size must be laid, and in order to preserve the life of a contact bed, it is advisable to retain as much as possible of the suspended matter upon

the surface of the material by using fine material for the top six inches or so.

In practice it has been found necessary in some instances to wash the filtering material when it has become clogged, and in a few of the larger installations this operation is carried on continuously. Not only has this to be done on account of accumulated solid matters derived from the sewage passed to the bed, but is in part due to the consolidation and disintegration of the material of which the bed is formed. Whether it is more economical frequently to wash or renew the material in contact beds, or to remove the greater portion of the suspended matters from the sewage liquid before it is treated and to wash the beds less frequently, depends primarily on local circumstances, yet it is important to state that the troubles arising from clogging are generally traceable to (a) the employment of inferior material forming the bed, (b) allowing too much suspended matter to be carried forward with the tank effluent, (c) overworking the filters. There is therefore a limit to the economical use of 'washery' plant in connection with the working of contact beds. The troubles that have been experienced in maintaining contact beds have led to their gradual conversion into percolating filters.

Percolating filters.—In percolating filters the sewage is not held up, but is allowed to percolate through the filter in the presence of air and the organisms on the surface of the filtering medium. Clinker and coke are preferable materials to form the filtering medium, presenting the roughest and most irregular surfaces.

The grading of the material is largely influenced by the presence or absence of suspended matters, and by the amount of 'removable' organic matter in the sewage effluent applied to the filter. In practice, material of $\frac{1}{4}$ inch diameter (fine material) is the smallest grade used for liquids containing little or no suspended matter, but the usual grade employed is not less than $1\frac{1}{2}$ ins. to 2 ins. diameter.

The most usual form of filter is circular in plan, this form being adopted because the distribution of the sewage is most frequently effected by means of revolving sprinklers which cover a circular area. The floor of the bed should be constructed of concrete of sufficient thickness to form an impervious stratum over which the drainings from the bed can flow. Upon this floor, a false tapered tiled floor is constructed, leaving air and drainage spaces between the tiles, aeration of the bottom part of the bed with effective drainage being essential in order to obtain a fully oxidised effluent and to enable the bed to excrete the solid matter which passes from it.

The external walls are usually constructed by honeycombed brickwork providing ventilation of the sides of the filters. The depth of the filter is controlled, on the one hand, by the strength of the sewage to be treated, and on the other hand, by the size of the filtering material, and it is generally assumed that a filter is capable of purifying a quantity of sewage proportionate to its depth.

Efficient and equable distribution of the effluent over the surface of the filter is essential, and there are many devices used for this purpose, the class of automatic revolving distributors

being mostly employed. The Candy-Whittaker distributor is capable of automatically dealing with any flow between 150 and 1600 gallons per square yard of bed per 24 hours without the employment of an automatic valve or dosing chamber. The effluent from percolating beds contains suspended matters of a humus character which it is essential to remove. Secondary sedimentation with or without shallow cinder filtration forms, therefore, an integral part of most percolating filter plants.

These humus tanks are being built larger than formerly—the aim being to provide a detention period of two hours during maximum flows at times of storm.

Percolating filters are better adapted to variations of flow than contact beds, and are less liable to become clogged.

The Royal Commission found that where the sewage effluent contains much suspended matter, it is usually advisable to construct percolating filters of coarse material, *whatever the strength of the original sewage*. Moreover, in nearly every case a greater rate of filtration can be adopted if the material is arranged in the form of a percolating filter than if it is used in contact beds. The rate of filtration per cube yard in the case of percolating filters may, generally, be double or nearly double that which is permissible in the case of contact beds.

Bio-aeration method.—This method, which is purely a tank treatment, depends primarily on the utilisation of sewage sludge itself as a carrier for the essential bacteria in place of the filtering or contact media generally employed.

An adequate supply of air and a fairly definite volume of 'conditioned' sludge (so-called 'activated' sludge) have to be maintained.

The sludge is kept in suspension and in circulation so as to mix intimately with the incoming flow of sewage. In some installations a forced air supply is relied upon for these purposes, but in others, surface aeration by paddles and congested flow channels fulfil the purpose. Details can vary so long as these two conditions are attained.

Through the results obtained with demonstration units the Ministry of Health has sanctioned loans for the construction of works to treat by this method the sewage flow of several towns (*see Annual Reports of the Soc. Chem. Ind. 1917–1922*).

Also for a review of the progress made with the 'bio-aeration' method of sewage purification, *see the Annual Reports of the Rivers Department of the Manchester Corporation, 1920–23* (E. Bartow and G. C. Baker, *J. Ind. Eng. Chem.* 1922, 14, 842; E. Ardern, Surveyor, 1922, 217; and J. Haworth, Surveyor, 1922, 198).

'During the past ten years, data have been collected at the Lawrence Experimental Station (Massachusetts State Board of Health) as to the part played by carbon compounds (other than carbonates) in sewage and sewage purification. Determinations of the carbon content and loss on ignition of evaporation residues, showed that in the case of residues from sewage, carbon formed, on the average, 33 p.c. of the total residue and 50 p.c. of the loss on ignition, the corresponding figures for residues from other

products being: surface waters, 7.5 and 26; sewage effluents from filters of coarse material, 10 and 36; wool scourings, 17 and 54; and paper mill waste, 23 and 61 respectively. The ratio of carbon to organic nitrogen in the different products was as follows: sewage, more than $11\frac{1}{2}$; surface waters, 16–20; sewage effluents, $6\frac{1}{2}$ – $7\frac{1}{2}$; wool scourings, 21; paper mill waste, $14\frac{1}{2}$. In a number of sewage sludges, nearly one-half of the organic matter consisted of fatty substances, and the carbon content of the sludge was about 55 p.c. of the loss on ignition. In sediments from trickling or contact filters, the carbon content was 50 p.c. of the loss on ignition. Septic tank sludge contains 56–61 p.c. of carbon, and the carbon content of the fatty substances therein is about 25 p.c. of the total carbon. In the case of sands from sewage filters, a considerable portion of the loss on ignition may be due to chemically combined water. In some specimens examined, the carbon content was 7–12 times as high as the organic nitrogen, and on the average was about 35 p.c. of the loss on ignition. Experiments were made to determine the maximum oxygen consumed by boiling with permanganate till no further reduction of the latter took place (8 hours usually sufficed), and the results were compared with the oxygen consumed in two minutes, and with the amount of oxygen theoretically necessary to oxidise the carbon content of the sewage, &c. In unfiltered sewage, the two minutes' "oxygen consumed" was 10–19 p.c. and the maximum "oxygen consumed" 34–54 p.c. of the theoretical value, whilst in filtered sewage, the corresponding figures were 13–28 and 51–86 p.c. respectively, and in effluents and waters the percentages were still higher. The clogging of sewage filters is due chiefly to non-nitrogenous carbon compounds (cellulose, fats, &c.). In the matter retained by the filters, the amount of carbon is about seven times as high as that of organic nitrogen. About 75 p.c. of the carbonaceous matter stored in the filter is contained in the first foot in depth. A study of nitrification in sewage has indicated that if the carbon content of the sewage is 10 times that of the nitrogen, nitrification will not take place. If the nitrogen content be increased, nitrification begins, but may again be checked by increasing the carbon content' (H. W. Clark and G. O. Adams, *J. Ind. Eng. Chem.* 1911, 3, 738–742).

Based upon the recommendations contained in the Fifth Report of the Royal Commission (1909), the Local Government Board adopted their revised and supplementary requirements (1909) with respect to sewage purification schemes (*Sanitary Engineering, Moore and Silcock, vol. 2, appendix iii.*).

Quantity of sewage to be treated.—The quantity of sewage per head of population is usually reckoned at the rate of 30 gallons per day for dry weather flow for domestic purposes. If there be trade refuse to be dealt with this must be added.

The quantity of sewage and rain-water to be *fully* treated at the works is: 3 times the domestic sewage plus $1\frac{1}{10}$ trade refuse, and the quantity of sewage and rainfall to be *partially* treated in storm beds is 3 times the domestic sewage plus $1\frac{1}{10}$ trade refuse. Any excess over

these quantities may be discharged over the storm-water overflows.

Storm overflows.—Storm overflows on sewers should as far as is reasonably practicable be avoided, but when they are necessary they should be placed in such positions and with the weirs so fixed that no nuisance is likely to result. In any district where there is an active river authority, the Board will desire to be informed of the opinion of such authority in respect of any proposed overflows. In the absence of any special circumstances, overflow weirs should be fixed so as not to come into operation until the flow exceeds six times that of the average dry-weather flow.

There should be no overflow for untreated sewage or storm-water at or near the disposal works.

Screens.—All liquid delivered at the disposal works should, as a rule, be passed through a screening chamber.

Storm-water treatment.—A weir set at three times the dry-weather flow should be placed below the screens, and any volume passing over this weir should be dealt with in storm tanks. The tanks should be two or more in number and their total capacity should not be less than a quarter of the dry-weather flow. They should be so arranged that when they are full they will act as 'continuous flow' tanks, and that they can be readily emptied and kept empty when no liquid is passing into them.

The liquor from the tanks can be discharged without further treatment except in special cases, and the sludge should be dealt with by any of the usual methods which may be most suitable in the particular circumstances.

In cases where a sufficient area of suitable land is available for the purpose, detritus tanks followed by irrigation may be substituted for the storm tanks.

SEWAGE TREATMENT.

Detritus tanks.—There should be two or more detritus tanks below the screening chamber. The capacity of each tank should be about $\frac{1}{10}$ of the dry-weather flow.

Septic tanks.—Septic tanks should not be less than two in number, and their total capacity should be about equal to the dry-weather flow.

Chemical precipitation tanks.—For *quiescent* treatment there should not be less than eight tanks, each of which should have a capacity equal to about two hours' dry-weather flow.

For *continuous flow* treatment there should not be less than two tanks, with a total capacity of at least eight hours' dry-weather flow, and in most cases a greater number of tanks will be desirable.

Settling tanks.—For *quiescent* treatment, same as chemical precipitation tanks.

For *continuous flow* treatment there should not be less than two tanks, with a total capacity of from 10 to 15 hours' dry-weather flow.

Filters.—In determining the sizes of percolating filters and contact beds, the Board have, in order to allow for the strength of the sewage

to be treated, adopted the divisions into 'strong,' 'average,' and 'weak' sewages recommended by the Royal Commission.

The strength of sewage should, when possible, be ascertained by analysing average samples of crude sewage taken in dry weather at frequent and regular intervals throughout seven days, and in proportion to the flow. Possibly, in the case of small works, the period for taking samples for analysis might be somewhat shorter, but the period should not be less than 48 hours, and Saturday and Sunday should be avoided.

In every case, the daily rainfall during the period when the samples were being taken and during the seven preceding days should be ascertained.

The analysis should, in all cases, include the following items: in parts per 100,000 by weight:—

1. Ammoniacal nitrogen.
2. Albuminoid nitrogen.
3. Total nitrogen.
4. Oxygen absorbed from strong permanganate in three minutes at 80°F. (3.94 grms. KMnO_4 per litre).
5. Oxygen absorbed from strong permanganate in four hours at 80°F.
6. Suspended solids.
7. Soluble solids.
8. Chlorine.

It is also desirable that the amount of dissolved oxygen taken up during the oxidation of the ammoniacal and organic matter of the sewage should be given.

The results of analysis would, of course, require to be properly interpreted; but as a rough guide, it may be taken that from the figure for 'oxygen absorbed from strong permanganate in 4 hours at 80°F.,' the strength of the sewage may be very roughly classified as follows:—

'Strong' sewage	17–25	parts per 100,000.
'Average' „	10–12	„ „
'Weak' „	7–8	„ „

In cases where the sewage cannot be analysed its strength should be estimated according to the water consumption, the flow per head, the kind of sewerage system, whether water-closets are in general use, the volume and nature of the trade waste, the amount of dilution by subsoil or surface water, &c.

Failing satisfactory evidence to the contrary, it will be desirable to assume that the sewage is 'strong' for the purpose of estimating the required capacity for the disposal works.

For the purpose of showing the *minimum* total cubic contents of filters required for treating three times the dry weather flow in different cases, the tables A and B have been prepared on the data given in the Commission's Report. Wherever possible, the figures are calculated from the data on pp. 117 and 118 of the Fifth Report, otherwise the calculations are based on the data in the tables between pp. 202 and 203.

The rates of filtration given by the Commission are rates which can generally be *doubled* in wet weather. Where it is proposed to deal with *three* times the dry-weather flow, the

Commission say that it would generally only be necessary to provide $1\frac{1}{2}$ times the capacity of filter required for the dry-weather flow (paragraph 293 of Report, 209). Hence the rates of filtration given by the Commission must be reduced by one-third to arrive at the basis for calculating the size of the filters for *three* times the dry-weather flow, and this reduction has been made in arriving at the figures in the tables.

TABLE A.—CONSTANTS FOR CALCULATING THE MINIMUM CUBICAL CONTENTS OF PERCOLATING FILTERS.

Preliminary treatment	Strong sewage		Sewage of average strength		Weak sewage	
	Coarse or medium material	Fine material	Coarse or medium material	Fine material	Coarse or medium material	Fine material
Detritus tanks	15	*	25	*	40	*
Septic tanks	45†	*	70	*	100	100
Settlement tanks (continuous flow) .	45†	*	70	*	100	100
„ „ (quiescent)	50†	25	100	70	130	130
Precipitation tanks (continuous flow)	65	50	100	80	150	175
„ „ (quiescent)	100	65	130	130	170	200

Notes as to filtering material.—(a) A filter may be regarded as ‘coarse’ if the material will not pass through a 1-inch sieve; as ‘medium’ if it will pass through a 1-inch but not through a $\frac{1}{2}$ -inch sieve; and as ‘fine’ if it will pass through a $\frac{1}{2}$ -inch sieve.

(b) ‘Coarse’ material will be desirable in

all cases where the liquid to be treated contains much suspended matter.

(c) In the cases marked *, the use of fine material would not be desirable unless the circumstances were exceptional.

If ‘medium’ sized material were used in the cases marked †, the figures should be reduced by about 10.

TABLE B.—CONSTANTS FOR CALCULATING THE MINIMUM CUBICAL CONTENTS OF CONTACT BEDS.

Preliminary treatment	Strong sewage			Sewage of average strength			Weak sewage		
	Single contact	Double contact	Triple contact	Single contact	Double contact	Triple contact	Single contact	Double contact	Triple contact
Detritus tanks	—	—	25*	—	25	†	—	38	†
Septic tanks	—	—	33	—	38	†	75*	66‡	†
Settlement tanks (continuous flow) .	—	—	33	—	38	†	75*	66‡	†
„ „ (quiescent)	—	—	44	—	50	†	100	†	†
Precipitation tanks (continuous flow)	—	33	†	—	50	†	133‡	†	†
„ „ (quiescent)	—	43	†	—	66*	†	133‡	†	†

Notes.—(a) The beds should not be less than 2 ft. 6 ins. nor more than 6 ft. in depth.

(b) The different series of beds, in double and triple contacts, should have equal cubic contents, failing any evidence to the contrary.

(c) Where a blank is left in the tables, the particular treatment indicated would only be desirable in exceptional circumstances, as the method would not generally be economical.

(d) In the cases marked thus †, the particular treatment indicated would only be necessary in

exceptional circumstances (*i.e.* when an unusually good effluent is required).

(e) Where three times the d.w.f. has to be dealt with in wet weather, the individual beds, in the cases marked ‡, should be small (to facilitate rapid filling and emptying) or the total cubic contents of the filters should be increased.

(f) The average liquid capacity of a cubic yard of contact bed is about 50 gallons. There are no data in the Commissioners’ report with regard to the cases marked thus *.

In order to ascertain the minimum total cubic contents of the filters required, divide the dry-weather flow by the appropriate figure (having regard to the strength of the sewage and the kind of treatment proposed) in the tables and the result will be the number of cubic yards which the filters should contain for treating up to three times the dry-weather flow, thus:—

Example 1.—A ‘strong’ sewage is to be

treated by means of ‘septic tanks’ and ‘percolating filters,’ of ‘coarse’ material, and the dry-weather flow is 90,000 gallons. The appropriate figure in Table A is 45—then $90,000 \div 45 = 2000$: the minimum total number of cubic yards which the filters should contain.

Example 2.—An ‘average’ sewage is to be dealt with by means of ‘quiescent settlement tanks’ and ‘double-contact beds,’ and the dry-

weather flow is 50,000 gallons—the appropriate figure in Table B is 50—then $50,000 \div 50 = 1000$; the minimum total number of cubic yards which the filters should contain; and as in most cases the two series of beds would have the same cubic contents, there would be 500 cubic yards in the 'primary' beds and an equal number in the 'secondary' beds.

The definitions of the different classes of sewage and filtering materials must be regarded as being of an elastic nature, and it may sometimes be found desirable to use intermediate figures between those given in the tables in order to ascertain the required cubic contents of the filters.

In cases where a sufficient area¹ of suitable land is used for irrigating the filtrate, it will probably suffice if the total cubic contents of the filters is half that provided for by the tables, but where the filter capacity is so reduced it may be necessary in wet weather to restrict the flow to the filters to about $1\frac{1}{2}$ times the dry-weather flow and to pass the remainder of tank liquor direct to the land.

Effluent tanks or filters.—Where the effluent from filters is not irrigated on land, tanks (with a capacity equal to about two hours' dry-weather flow and with provision for removing sludge) or shallow straining filters, will in most cases be necessary for the purpose of preventing the suspended matters in the filtrate from passing into the river.

Sludge disposal.—The disposal of the sludge resulting from the preliminary treatment of sewage is the *bête noir* of the sewage problem, especially in the case of large towns or cities not situated on or near the sea-board. For small works not situated in the near vicinity of dwelling-houses, land drying or lagooning is, as a rule, advisable, the dried sludge being disposed of to farmers or by digging it into the soil. For medium-sized works, trenching in the ground is preferable, and for large inland works with a limited land area, preliminary treatment of the sludge by filter pressing is desirable before disposal to farmers, or on to land, or by burning with town refuse. At Harburg-on-Elbe and at Frankfort-on-the-Main, plants for sludge drying by centrifugals have been installed (Engineering, 1909), the dried sludge at the latter place being burned in a destructor in connection with the town refuse. The utilisation of sewage sludge as a fertiliser, or as a base for an artificial manure has not made much progress, the main technical difficulty being the de-watering of the sludge sufficiently to enable a portable product to be manufactured at an economical cost.

At Bradford, where the sewage contains a considerable quantity of wool-scouring liquid, the recovery of the grease from the sewage has been so far successful that the return from the sale of the products more than meets the working expenses of the tank treatment. The sewage, after screening, is treated with sulphuric acid in such quantity that there is an excess equal to 10 parts H_2SO_4 per 1,000,000. The acid sewage is subsequently passed through settling tanks. The sludge is removed from the settling tanks into cast-iron vats, where a further

quantity of sulphuric acid is added, and the temperature of the sludge is raised by steam to 100° . It is then run into steel rams and forced by compressed air into filter presses heated by steam, and the process of pressing is continued from 12 to 24 hours, hot sludge and steam being alternately admitted to the press. The pressed liquor, consisting of water and fat, is run into special vessels for the separation of the fat, after which the fat is boiled with acid and black oxide of manganese, in order to bring it into a marketable condition.

The amount of wet sludge produced in a year is about 100,000 tons. It contains about 80.15 p.c. of water, and 7.43 p.c. of grease, which is equivalent to 37.7 p.c. of grease on the dry matter.

The amount of pressed cake produced in a year is about 20,000 tons. This contains about 27 p.c. of water. Part of the pressed cake is used for fuel and is burnt in specially constructed brick furnaces; the fuel value is about 1s. 6d. per ton. Part is sold to farmers at 3s. 6d. per ton on rail at the works. Another portion is disintegrated and sold as manure at 5s. 6d. per ton, whilst 6s. 3d. per ton is obtained for the driest portion of the disintegrated pressed cake.

Tests for sewage effluents in relation to standards. The Royal Commission (8th report) recommend a normal standard. This standard should apply to all sewage discharges into non-tidal waters, except where local circumstances are shown to justify a special standard. A normal standard effluent should not contain more than 3 parts of suspended matter per 100,000, and that, including its suspended matters, it should not take up more than 2 parts of dissolved oxygen per 100,000 in 5 days at 65° Fahr.

A claim for a relaxed standard may be entertained under the following conditions:—

(a) When it can be shown that the particular river water is of such quality and volume that, when mixed with a sewage or sewage liquor of known or calculated strength and volume, it does not take up more than 0.4 part per 100,000 of dissolved oxygen in 5 days; and

(b) When there is reason to suppose, or when it can be shown that the river will receive no further pollution until it has recovered itself so far as not to take up in 5 days an amount of dissolved oxygen much in excess of that which it took up before receiving the first discharge.

F. S.

SEWAGE FATS. Sewage water (waste water from households, abattoirs, &c.) contains fatty matter in the form of soap, unsaponified fat, free fatty acids, and unsaponifiable matter. As sewage water is of an extremely putrescible nature, sanitary conditions require its immediate removal (from houses, &c.) and both rapid and careful treatment at the sewage works, so as to render the effluent innocuous in a manner best adapted to local conditions.

Up to about the beginning of this century no attempt had been made to recover the fatty matter. In the precipitation processes, which are employed to a great extent, the fatty matter is deliberately wasted, and one of the chief features of the biological ('digestive') processes is to destroy the fat as completely as possible by making it serve as a foodstuff for the bacteria

¹ Viz. from 3000 to 30,000 gallons (dry-weather flow) per acre per twenty-four hours according to the quality of the land.

which digest the fatty matter contained in raw sewage.

Of recent years, however, endeavours have been made, on a large scale, to recover the fatty matter contained in the sewage. Most of the recovery processes are designed on the lines of the methods practised in the wool, cotton, and silk industries, and especially in the recovery of wool grease from wool scourers' suds. (For further details of these processes, *cp.* Lewkowitsch, Chem. Tech.)

The composition of 'sewage fats' must vary with the localities whence they originate. Owing to the exceedingly favourable conditions for the micro-organisms thriving in raw sewage, the bulk of the neutral fat discharged into the sewage is hydrolysed; therefore 'sewage fats' are characterised by large proportions of free fatty acids. The amount of unsaponifiable matter is also considerable. The nature of the unsaponifiable matter has not yet been investigated. Probably it consists to a large extent of coprosterol, which forms an important constituent of excrementitious matter.

Judging from the composition of sewage fats it is evident that the products cannot pay the expenses of the process, unless, indeed, the recovery of the fat form an integral part of the sewage disposal process. J. L.

SHAKUDO. Shakudo is an alloy consisting essentially of copper and gold, which is used in Japan for the manufacture of objects of art, and is coloured by treatment with aqueous solutions containing copper sulphate and acetate. The coloration is due to the production of a layer of cupric oxide, the tint being determined by the thickness of the layer. The colouring solution contains hydrogen ions owing to hydrolysis of the copper salt, and when the alloy is introduced a local electrical circuit is formed between the gold and copper, the latter being dissolved as cupric ion and hydrogen ions being discharged, thus disturbing the equilibrium. In consequence of this, hydrolysis proceeds further, and the process goes on, with progressive increase of the concentration of cupric and hydroxyl ions, until the solubility product of cupric hydroxide is exceeded. The precipitated hydroxide is rapidly converted into the oxide, which is deposited on the surface of the alloy. An analogous coloration can be obtained on alloys containing palladium, platinum, and silver, respectively, in place of gold (S. Miyasawa, J. Chem. Ind. Tokyo, 1917, 20, 109, 365; J. Soc. Chem. Ind. 1917, 36, 884).

SHALE (*Schiste*,¹ *Schiste argileux*, Fr.; *Schieferthon*, Ger.). A general term applied to sedimentary rocks possessing a marked laminated structure parallel to the bedding planes, and thus distinct from slate (*q.v.*). Frequently they are argillaceous, consisting of clay or mud consolidated by superincumbent pressure; but with variations in composition they may pass into sandstone, limestone, clay-ironstone, coal, &c. Ordinary argillaceous shales, such as those of the Coal Measures and Lias, are ground for brick making; sandy shales and fireclay-shales are used for fire-bricks and refractory materials; calcareous shales for the manufacture of Portland cement

and hydraulic mortar; the pyritous alum-shales (*q.v.*) for the manufacture of alum. Other varieties of considerable commercial importance are carbonaceous, bituminous, and oil-shales (*v.* PETROLEUM). L. J. S.

SHALE OIL *v.* PARAFFIN.

SHANGHAI OIL. A variety of colza oil *v.* OILS, FIXED, AND FATS.

SHARK LIVER OILS. The hydrocarbon *iso*-octadecane $C_{18}H_{38}$, isolated by Tsujimoto from one sample of the liver oil of the giant shark (*Cetorhinus maximus*, Gunner) was isolated from the liver oils of the following species of shark: Rabukazame (*Clamydoselachus anguineus*), Kanatsubozame (*Scymnorphinus licha*, Bonnaterre), Kimbeizame (*Lepidorhenus kimbei*, Tanaka), Aizame and Kurozame. It was also isolated from another sample of the liver oil of the giant shark. This saturated hydrocarbon is therefore a general constituent of various liver oils containing squalene, and is named *pristane*. The following characters of pure pristane were determined: $n^{15}=1.4410$, $n^{20}=1.4390$; sp.gr. 0.7871 at $15^{\circ}/4^{\circ}C.$, 0.7835 at $20^{\circ}/4^{\circ}C.$; b.p. $158^{\circ}C.$ at 10 mm., $187^{\circ}C.$ at 30 mm., $296^{\circ}C.$ at 760 mm. without decomposition. Absolute viscosity at $30^{\circ}C.$, 0.443. It is optically inactive and easily soluble in benzene, chloroform, carbon tetrachloride, ether, petroleum spirit, warm acetone, and warm ethyl alcohol; somewhat difficultly soluble in cold acetone and ethyl alcohol; difficultly soluble in cold, but fairly easily in warm acetic acid; difficultly soluble in cold and fairly difficultly in warm methyl alcohol. The crude pristane obtained by fractionally distilling the oil is always contaminated with a small quantity of unsaturated hydrocarbons. It is doubtful whether these are original constituents of the oil or whether they are products of the decomposition of squalene. See SQUALENE (Y. Toyama, Chem. Umschau, 1923, 30, 181-187; J. Soc. Chem. Ind. Aug. 31st, 1923, 840, A.).

For the unsaponifiable constituents (higher alcohols) of shark and ray liver oils, see Toyama (Chem. Umschau, 1924, 31, 153; J. Soc. Chem. Ind. 1924, 43, B. 719). The oil from the Jewfish (*Stereolepis ischinagi*, Hilg.) contains a large amount of peculiar unsaponifiable matter (up to 50 p.c.), which is a viscous substance of reddish-orange colour, having a resinous odour, and showing much resemblance to colophony when dried at 100° for several hours. The name "liver-resin" is proposed for it. Liver oil from *Erilepis zonifer* (Lock.) also contains a similar substance (about 4 p.c.). These oils and the unsaponifiable matter (especially in carbon disulphide solution) give a deep violet coloration with sulphuric acid. With a sample of *S. ischinagi* liver oil, the coloration was observed to be about 100 times as strong as that of a cod-liver oil (M. Tsujimoto, J. Chem. Ind. Japan, 1923, 26, 482; J. Chem. Soc. Abstr. 1924, 126, i. 239).

The acetyl ester of the oleic alcohol obtained from Rabukazame (*Clamydoselachus anguineus*) liver oil gave on oxidation with potassium permanganate nonylic acid and acetylhydroxynonylic acid. This result, coupled with the previously established fact that the same substance gives the acetyl ester of *n*-octadecyl

¹ In English the name schist, from $\sigma\chi\acute{\iota}\zeta\epsilon\iota\nu$, to split, is limited to the crystalline schists, *e.g.* mica-schist.

alcohol on hydrogenation, establishes the formula of oleic alcohol to be



It is accordingly identical with the alcohol obtained from ethyl oleate. For purposes of comparison oleic alcohol and elaidic alcohol were prepared from ethyl oleate and ethyl elaidate respectively. The specific gravity and the refractive index of the former preparation were identical with those of the oleic alcohol obtained from Rabukazame oil. The following values were obtained: d_4^{15} 0.8523, d_4^{20} 0.8491, d_4^{40} 0.8367; $n_D^{15} = 1.4626$, $n_D^{20} = 1.4607$, $n_D^{40} = 1.4530$; b.p. 330°–335°. The elaidic alcohol gave m.p. 35.0°–35.5°, d_4^{40} 0.8338, $n_D^{40} = 1.4522$, b.p. about 330°. These two isomeric alcohols are very similar and showed no tendency to change into one another on heating or acetylation. They are sharply differentiated from one another by their melting points, as oleic alcohol does not solidify when cooled with ice-water (Y. Toijama, Chem. Umschau, 1924, 31, 13; J. Soc. Chem. Ind. 1924, 43, B. 223).

SHATTUCKITE *v.* DIOPTASE.

SHEA BUTTER *v.* BASSIA OILS.

SHĒ-CHUANG-TZU. A Chinese drug. The fruit of *Selinum Monnieri*, L. By steam distillation yields 1.3 p.c. of essential oil, containing *l*-pinene, camphene, and *l*-bornyl isovalerate (Manzō Nakao, J. Pharm. Soc. Japan, 1920, 685).

SHELLAC *v.* RESINS. The grading of shellac is based upon freedom from resin and dirt and upon the colour of the flakes. Resin is the most common adulterant. The best grades of shellac are free from resin, but a common grade containing 3–5 p.c. (added to facilitate the melting of the seed lac) is useful for many purposes. Lower grades of shellac contain higher percentages of resin. From 0.05 to 0.25 p.c. of orpiment is usually added in the manufacture of shellac, and tends to give the flakes a lighter appearance. Orange shellac, sp.gr. 1.08 to 1.13, is soluble in cold methyl or ethyl alcohol or a mixture of the two (denatured alcohol), but high-proof alcohol must be used (not below 95 p.c. by vol.), also in isopropyl and amyl alcohols, but quite insoluble in petroleum hydrocarbons or turpentine, thereby differing from all other common resins soluble in alcohol. It is very stable. In making shellac varnish completely denatured alcohol, 190° proof, should be employed, or the special denatured alcohol specified in U.S. Internat. Revenue Bureau, formula No. 1, consisting of 20 parts by vol. of ethyl alcohol, 190° proof, and 1 part by vol. of approved methyl alcohol (wood alcohol). The resin should be left overnight in contact with the proper volume of alcohol, and the mixture then stirred at intervals. Powdered resin partially oxidised through exposure to air does not give the Liebermann-Storch reaction, but gives the Halphen-Hicks reaction (J. 1911, 373), and the resin in shellac decreases in iodine value with increased age due to partial oxidation. Wijs's method is not applicable to shellac varnish, as the alcohol interferes with

the determination. The estimation of resin from the iodine value is unreliable, because the iodine value of resin is dependent upon the weight taken. For the detection and determination of adulterants in shellac a modification of the McIlhiney's method (J. 1908, 579) may be used. Shellac or shellac varnish is heated with acetic acid until the resin and wax are dissolved. The solution is then cooled to 19°–21°C., whereupon a part of the wax separates. Petroleum ether is then added and the shellac precipitated with water. An aliquot part of the petroleum ether layer is evaporated to dryness, and the residue dried until constant in weight, after which it is dissolved in a mixture of equal volumes of 95 p.c. denatured alcohol and benzol, and its acid value determined. The remainder of the petroleum ether layer is evaporated to dryness and tested for resin by the Halphen-Hicks method. Pure shellac yields 6–7 p.c. of material soluble in petroleum ether, with acid value 60–90, but shellac adulterated with resin gives more than 7 p.c. of soluble material and a higher acid value. If the shellac contains unoxidised resin, the excess of soluble material is approximately the percentage of resin present, but, if it contains oxidised resin, the difference represents the minimum of adulteration. The turpentine film test used by H. A. Gardner consists in flowing the sample of varnish on a strip of tin plate, allowing the coating to dry, immersing in turpentine overnight, and noting the condition of the film. A removal of the film indicates gross adulteration, but this test is only of value when positive, because grossly adulterated samples are sometimes unaffected. Shellac normally contains a small percentage of mineral water, which may be determined by heating the finely ground sample with 95 p.c. specially denatured alcohol No. 1 (*cf. supra*) until the resin and wax are dissolved. The boiling solution is filtered through a Gooch crucible, and the residue washed and dried at 105°–110°C. until constant in weight. Pure shellacs usually show less than 1.5 p.c. of material insoluble in hot alcohol, adulterated shellacs 1.5–2.0 p.c. The insoluble matter must not exceed 1.75 p.c. Samples of shellac which offer difficulty to filtration through a Gooch crucible should be continually extracted with hot alcohol in Knoefler's apparatus. Non-volatile matter in shellac varnish is determined by heating the varnish at 100°–105°C. till constant in weight. The ratio of shellac to solvent is obtained by distilling the varnish until nearly dry, taking the specific gravity of the distillate and calculating the pounds of shellac per gallon of alcohol from the formula, $y = ab(100 - b)$, where a is the weight of a gallon of alcohol in lbs.; and b is the percentage of non-volatile matter (P. H. Walker and L. L. Steele, U.S. Bureau of Standards, Techn. Paper No. 232, 1923, 17, 277; J. Soc. Chem. Ind. June, 1923, 563, A).

Pure shellac can be obtained from the natural product by repeated shaking with ether, in which the accompanying substances are soluble. After several precipitations from alcohol the pure resin is obtained, but although the product has always the same colour, yet sometimes it is insoluble in alcohol. If the

insoluble variety is dissolved in acetic or formic acid and the solution treated with water, the shellac is precipitated in a form which is soluble in alcohol. Ordinary shellac is hydrolysed by potassium hydroxide to give 22 p.c. of the potassium salt of aleuritic acid, whereas the product insoluble in alcohol is either not hydrolysed in this way or only to the extent of 12 p.c. The insoluble product which has been rendered soluble by solution in acetic acid is also only slightly hydrolysed (3 p.c.) by potassium hydroxide. If, however, this product is dissolved in alcohol and precipitated by water, it reverts to the original form, which yields 22 p.c. of aleuritic acid on hydrolysis. The three forms have practically the same colour; the insoluble product shows no change on heating to 240°C., but the product which has become soluble in alcohol is coloured at 102°C., shows strong sintering, and gradually melts. The composition of the three varieties is identical. The change from the ordinary variety to the insoluble variety is brought about by shaking 100 grms. of the ordinary resin dissolved in 1000 c.c. of ether with 2 c.c. of concentrated hydrochloric acid solution (C. Harries and W. Nagel, *Kolloid Zeitsch.* 1923, 32, 247-248; *J. Soc. Chem. Ind.* 1923, 42, 1234 A).

On the nature of shellac, see C. Harries and W. Nagel (*Ber.* 1922, 55, [B] 3833-3848; *J. Chem. Soc.* 1923, 123, 124, i. 120).

On treating shellac with 5*N* potassium hydroxide in the cold for 12 hours it yields the potassium salt of aleuritic acid. By acting on this with dilute sulphuric acid and recrystallisation from ethyl acetate and alcohol the pure acid is obtained, m.p. 100°-101°. It is reduced to palmitic acid by the action of hydriodic acid. It is therefore trihydroxy-palmitic acid and not dihydroxytridecylic acid as stated by Tschirch (*Die Harze u. Harzebehälter* ii. 251); Harries and Nagel (*Chem. Umschau*, 1922, 29, 135).

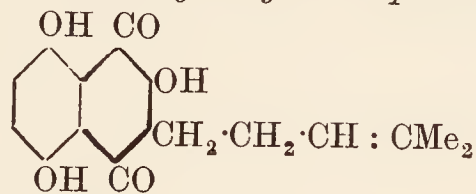
Stick-lac.—Indian stick-lac is a gum or resin formed by a species of louse, *Tachardia lacca*, parasitic on certain trees in the East. Extraction of the lac with cold water removes sugars, albumin, and the dyestuff *laccaic acid*. Further extraction with cold alcohol removes a second dyestuff, *erythrolaccin*, the resinous constituents, and an odoriferous substance. The waxes are then extracted successively with boiling alcohol and benzene, leaving as residue only the skeleton of the *tachardia* with a little adsorbed *laccaic acid*. The sugars appear to be invert sugar, formed from the sucrose of the tree by the action of an enzyme in the *tachardia*. The dyestuff, *laccaic acid*, is an anthracene derivative of unknown constitution; its formula is probably $C_{20}H_{14}O_{10}$ (*cf.* Dimroth and Goldschmidt, *Annalen*, 1913, 399, 62). It forms stout red crystals, soluble in water, and dyes wool and silk from an acid bath in orange-red shades, remarkably fast to light. The shades are modified by inorganic salts (mordants), ammoniacal copper giving a bluish violet, lead acetate a reddish violet, potassium bichromate a reddish yellow, calcium and barium salts carmine-red, etc. It forms corresponding lakes with these salts. The dye is a sensitive indicator, being yellow in acid and violet in alkaline solution. Its alkaline solutions are unstable. The second dyestuff, *erythrolaccin*,

is yellow, turning violet in presence of alkali, and forming a violet lake with lead acetate; its alkaline solutions are unstable. It crystallises in yellow leaflets of the composition $C_{15}H_6O_2(OH)_4 \cdot H_2O$, but loses H_2O at 105°. It forms a *tetra-acetyl* derivative, and appears to be a tetrahydroxy-methylantraquinone. The resinous constituents of the stick-lac give when hydrolysed a mono- and a trihydroxy-palmitic acid and other unidentified acids. These are probably present in the lac as lactides. The wax extracted by boiling alcohol has m.p. 82°, and can be hydrolysed into an alcohol, *tachardiacerol*, $C_{24}H_{50}O$, m.p. 82°, and an acid, m.p. 74°-76°. The wax soluble in benzene contains an alcohol, termed *laccerol*, $C_{32}H_{66}O$, m.p. 88°, and an acid, *lacceric acid*, $C_{32}H_{64}O_2$, m.p. 95°-96° (*cf.* A., Jan.; A. Tschirch and F. Lüdy, jun., *Helv. Chim. Acta*, 1923, 6, 994-1008; *cf.* Tschirch and Farner, *Arch. Pharm.* 1899, 35; *J. Chem. Soc.* 1899, i. 446; *J. Soc. Chem. Ind.* 1924, 43, B. 103).

SHIBOUL. *Kakishibu*, the pale yellow, cloudy extract of unripe kaki fruit, contains a phenolic substance, $C_{14}H_{20}O_9$, probably a phlobatannin, for which the name *shibuol* is proposed. Shiboul (1-2 p.c.) may be obtained from kakishibu by precipitation either with a mixture of alcohol and ether, or with acetic acid, or with concentrated hydrochloric acid or with basic lead acetate. It is converted, when fused with potassium hydroxide, into gallic acid, phloroglucinol (49.7 p.c.), and a substance, $C_{12}H_8O_5$.

Kakigoma $C_{11}H_9O_5$, a brown, amorphous substance, obtained from the pulp of the dried fruit *dojo-hatiya*, after purification by extraction with sulphuric acid, is soluble in alkalis, insoluble in organic solvents, and, on fusing with potassium hydroxide, gives phloroglucinol (17.88 p.c.), gallic acid, and a substance, $C_{13}H_9O_5$ (Shigeru Komatsu and Naohiko Matsunami, *Mem. Coll. Sci. Kyoto Imp. Univ.* 1923, 7, 15; *J. Chem. Soc. Absts.* 1923, 124, i. 1197).

SHIKON. The dried roots of *Lithospermum erythrorhizon*. The colouring matter is the monoacetyl derivative of shikonin $C_{16}H_{16}O_5$, m.p. 147°. Its constitution is that of δ -methyl- $\Delta\gamma$ -pentenyl-2:5:8-trihydroxy-1:4-naphthaquinone



On heating, shikonin is partly converted into *shikazarin* (1:4-dihydroxy-8-methylantraquinone), m.p. 232°, and on dry distillation gives 1- and 2-methylantraquinones. Shikazarin distilled with zinc-dust gives the same products. Oxidised with potassium permanganate in acetone solution, shikazarin gives 3-methylphthalic acid.

Shikonin forms sodium and copper salts, and on acetylation forms a *triacetyl* derivative, m.p. 113°, but if the acetylation is carried out in presence of zinc-dust, a *penta-acetyl* derivative of reduced shikonin, m.p. 90°, is produced, which on bromination gives a *bromo-compound*, $C_{16}H_{12}O_5BrAc_5 \cdot H_2O$, m.p. 123°. Shikonin forms a *dibenzoyl* derivative, m.p. 168°, and an oxime, m.p. 163° (Rikô Majima and Chika Kuroda, *Acta Phyto-chim.* 1922, 1, 43).

SHINNAMU. A vegetable dye obtained from a species of maple found at Kaijo (Song-do) and elsewhere in Corea.

SIDERITE (Lat. *Siderites*; Gr. *σιδηρίτης*, from *σίδηρος*, iron), *v.* CHALYBITE. This name has been applied to minerals of several kinds; and unfortunately it is still in common use in two distinct senses, namely, for the rhombohedral ferrous carbonate chalybite (*q.v.*), and for the group of meteoric irons. In the former sense it was first used by F. S. Beudant in 1832 in the form *sidérose*, which was altered by W. Haidinger in 1845 to *siderit*. This has priority over the name chalybite (E. F. Glocker, 1847), and it is also in more frequent use, especially in America and France; but it has the objection that it has other applications. The meteoric irons, composed mainly of nickel-iron alloys, were grouped by N. S. Maskelyne in 1863 under the name *aerosiderites*, which was shortened to *siderites* by G. A. Daubrée in 1867; any particular individual being referred to as a *siderite*. Originally the name *siderite* was no doubt used in general for iron-stone or iron-ores, and in particular for loadstone (*q.v.*). T. O. Bergman in 1790 adopted it for the mineral now known as pharmacosiderite (hydrated basic ferric arsenate), and J. Pinkerton in 1811 used it for hornblende. Finally, the same name has been applied to a number of minerals with a blue colour; by Pliny to a precious stone, probably sapphire; lazulite (basic aluminium, magnesium, and ferrous phosphate); sapphirine (basic aluminium magnesium silicate); and deep-blue quartz ('sapphire-quartz'); the last of these, due to C. v. Moll (1797), being still in current use. In botany, 'siderite' or iron-wort is a plant of the genus *sideritis*. L. J. S.

SIDONAL. Piperazine quinate. Used as a uric acid solvent.

SIDONAL, NEW. Trade name for a mixture of quinic acid and quinic anhydride.

SIEMENS STEEL *v.* IRON.

SIENNA *v.* PIGMENTS.

SIFLURAL. Trade name for a solution of aluminium fluosilicate. Used as a disinfectant.

SILBEROL *v.* SYNTHETIC DRUGS.

SILEX, SILICA, *v.* SILICON.

SILFRAX or **SILICIDISED CARBON** is obtained by the action of the vapour of silica or silicon on carbon and consists of carbon penetrated to a depth of about $\frac{1}{2}$ in. with silicon carbide. Silfrax differs from carborundum in the mode of its production being formed mainly by the action of silicon vapour on carbon *in situ*, and not from gaseous carbon compounds. It has a toughness and mechanical strength superior to carborundum and is used as a refractory material for the manufacture of pyrometer tubes, electrical heating elements and chemical ware (Tone, Trans. Amer. Electrochem. Soc. 1914, 26, 181).

SILICAL. Kautsky's term for the radicle Si_2OH . Forms a *bromide*, Si_2OHBr , which on treatment with water yields *silical hydroxide*, a red compound which combines with acids to form salts, yellow to red in colour. They are powerful reducing agents and are decomposed by alkalis with evolution of hydrogen and formation of silica (Kautsky, Zeitsch. anorg. Chem. 1921, 117, 209).

SILICATE COLOURS *v.* PAINTS AND PIGMENTS.

SILICATE PAINTS *v.* PAINTS AND PIGMENTS.

SILICIOUS CEMENTS *v.* CEMENT.

SILICIOUS SINTER *v.* GEYSERITE.

SILICON. Sym. Si. At.wt. 28.11; 28.15 (Stock and Kuss); 28.06 (Baxter, Weatherill and Scripture). According to Aston, silicon has atoms of isotopes whose mass is twice the atomic number. Silicon is not found in the free state in nature, but occurs abundantly as silica and metallic silicates. It is known in the following modifications:—

1. **Amorphous silicon**, first obtained by Berzelius (1823) by heating dry potassium or sodium silico-fluoride with an equal weight of potassium or sodium respectively.

By passing the vapour of silicon chloride over potassium or sodium heated in a porcelain boat, or over heated aluminium (Hautefeuille and Perrey, Compt. rend. 100, 1220).

By passing silicon fluoride over metallic sodium at 400°–500°, and heating the powdered product with sufficient sodium to decompose any sodium silico-fluoride formed, and with aluminium in sufficient quantity to form an alloy of not more than 16 p.c. Si. The residue after treating with hydrochloric acid is lead grey in colour, and contains 3–4 p.c. of silica. On extracting with hydrofluoric acid, brown amorphous silicon is obtained in a very reactive form (Hempel and v. Haasy, Zeitsch. anorg. Chem. 1900, 23, 32).

By heating magnesium powder and silica in the requisite proportions in presence of magnesia to moderate the action. The product is heated successively with dilute hydrochloric and sulphuric acids, then treated two or three times alternately with hydrofluoric and sulphuric acids, and finally with hydrochloric acid. Thus obtained, it is a maroon-coloured powder, containing only 0.4–1 p.c. impurity. Aluminium may be used instead of magnesium (Vigouroux, Compt. rend. 1895, 120, 94, 1161). If kieselguhr or precipitated silica is used, reaction takes place with aluminium in the cold (Weston and Ellis, Trans. Faraday Soc. 1908, 3, 170).

By sparking liquid silicon hydride (Moissan and Smiles, Compt. rend. 1902, 134, 1552).

By electrolysis of a fused mixture of potassium fluoride and silicofluoride.

For other electrolytic methods, *v.* Gore (Chem. News, 50, 113), Warren (*ibid.* 57, 54), Hampe (Chem. Zeit. 12, 841).

This form of silicon is a brown or maroon-coloured powder, sp.gr. 2.35 at 15°; fuses at 1420° and volatilises in the electric furnace, dissolves in many molten metals, readily absorbs gases and water vapour, which can only be expelled at red heat; is not attacked by iodine, combines with bromine at 500°, chlorine at 450°, and with fluorine at ordinary temperatures with incandescence; oxidises superficially in air, burns in oxygen at 400°, combines with nitrogen at 1000°, and becomes incandescent in sulphur vapour at 600°; halogen acids attack it at dull red heat, but concentrated hydrofluoric acid at 100° has no action; reduces carbon dioxide to carbon monoxide at 800° (Vigouroux, Compt. rend. 120, 367; Cambi, Atti R. Accad. Lincei, 1911, [v.] 20, i. 440).

It is attacked by hot water in glass vessels,

which explains the poor yield with many workers, and when heated with hydrofluoric acid becomes much more reactive, being violently attacked by concentrated nitric acid (Wilke, Dörfurt Festschrift Otto Wallach, 1909, 671).

It reduces many metallic fluorides and oxides below red heat. As prepared by sparking silicon hydride it is capable of reducing salts in solution.

2. Graphitoidal silicon. By strongly heating amorphous silicon in a platinum crucible (Berzelius). By electrolysis of sodium aluminium chloride and extraction with hydrochloric acid (Deville). By strongly heating a mixture of aluminium with 20 to 40 times its weight of potassium silicofluoride; after successive treatment of the product with hydrochloric and hydrofluoric acids, graphitoidal silicon remains in the form of hexagonal tables with curved edges (Wöhler, *Compt. rend.* 42, 48).

By fusing the product obtained on heating a mixture of finely powdered sand and magnesium in a test-tube, with aluminium and cryolite. On treatment with water and acids, black glistening spangles of graphitoidal silicon remain (Hyde, *J. Amer. Chem. Soc.* 1899, 21, 663).

Also by fusing aluminium (1 part) with glass free from lead (5 parts) and cryolite (10 parts), and treating successively with hydrochloric and hydrofluoric acids; sp.gr. 2.49. Unaltered in oxygen at white heat, but burns brilliantly when heated to redness with potassium carbonate, although only at white heat with the chlorate or nitrate. Unattacked by acids, except by a mixture of nitric and hydrofluoric acids. Soluble in strong potash or soda; combines with chlorine at red heat, and with fluorine at the ordinary temperature. It reduces many metallic oxides, in some cases with explosive violence (Warren, *Chem. News*, 64, 75).

3. Crystalline or adamantine silicon is obtained according to Deville on heating amorphous silicon in a platinum crucible lined with lime to a temperature between the melting-points of steel and cast-iron, in dark, steely grey globules, sometimes yielding double six-sided pyramids (*Ann. Chim.* [3] 49, 68).

When silicon chloride vapour is passed over aluminium fused in an atmosphere of hydrogen, a portion of the aluminium is volatilised as chloride, and the remainder becomes saturated with silicon. At the point of saturation the excess of silicon separates in large needles of dark iron-grey colour, reddish by reflected light, and iridescent. The form is derived from a rhombic octahedron, and the crystals often exhibit curved faces. They are capable of cutting glass.

By heating to redness in a clay crucible, a mixture of potassium silico-fluoride (3 parts), sodium (1 part), and zinc (4 parts). The zinc is removed by fusing and then by successive treatment with hydrochloric and boiling nitric acids, leaving the crystalline silicon in long needles (Deville and Caron, *Ann. Chim.* [3] 63, 26; *ibid.* [3] 67, 441; Robins, *Chem. News*, 5, 102); v. also Kühne (*D. R. P.* 147871); Hollemann (*Proc. K. Akad. Wetensch. Amsterdam*, 1904, 7, 189).

It is most conveniently obtained by the action of aluminium upon potassium silico-

fluoride. The product, purified in the usual way, still contains traces of iron, and Vigouroux (*Bull. Soc. chim.* 1907, [iv.] 1, 16) has obtained it in a pure condition by digesting for some time with diluted hydrofluoric acid (1:1) in a platinum vessel, and then with concentrated sulphuric acid, these processes being repeated until no residue is left on evaporation with a mixture of nitric and hydrofluoric acids.

The identity of amorphous and crystalline silicon according to Manchot has been proved by an X-ray examination by Debye and Frauenfelder (*Zeitsch. anorg. Chem.* 1922, 124, 333). The two forms can be distinguished by rubbing them with lead peroxide, when the pseudo-amorphous variety ignites, the brown form exploding.

The crystal structure of the various forms of silicon has been determined by means of X-rays by H. Kuestner and H. Remy (*Phys. Zeits.* 1923, 24, 25-29), specimens with between 2.5 and 30 p.c. of SiO_2 all showed the diamond structure, as discovered by Debye and Scherrer, 'amorphous silicon,' containing 72 p.c. SiO_2 showed only the spectrum of quartz. There was in no case any evidence of the existence of amorphous silicon. Difference of chemical reactivity was shown to be due to the amount of surface exposed, being greater with fine particles than with large ones. The edge of the elementary lattice cell (100) of silicon measures $5.4204 \pm 0.00016 \text{ \AA}$.

Crystalline silicon is less reactive than amorphous silicon, although by rapidly heating in oxygen it may be made to take fire at 400° . It is also attacked, if finely divided, by boiling water, but not in fused quartz or platinum vessels (Moissan and Siemens, *Compt. rend.* 1904, 138, 939).

Another *modification* is described by Moissan and Siemens (*ibid.* 1904, 138, 1299). It is obtained mixed with the ordinary crystalline form from a solution of silicon in molten silver, in which it is very soluble (41.66 p.c. at 1470° , 9.22 p.c. at 970°). Yield is 99 p.c. from a 2 p.c. solution, decreasing with increasing amounts of silicon. It is readily attacked by hydrofluoric acid, thus differing from other modifications: sp.gr. 2.42, v. also Warren (*Chem. News*, 67, 136).

Silicon as such has received no important commercial application, but Le Roy (*Compt. rend.* 1898, 126, 244) recommends it for electrical heating in place of metallic and carbon resistances. A rod, 10 cms. long and 40 sq. mm. cross section, has a resistance of 200 ohms, that of a similar carbon rod being 0.15 ohm.

For its position in the thermo-electric series see Fischer and Baerwind, *Physikal. Zeitsch.* 1916, 17, 373; *Zeitsch. anorg. Chem.* 1916, 97, 56.

Silicon steel v. IRON.

For the spectra of silicon and its compounds, v. Wesendonck (*Wied. Ann.* 21, 427); Hartley (*Chem. Soc. Trans.* 1883, 397; *Proc. Roy. Soc.* 1901, 68, 109); Lunt (*ibid.* 1900, 66, 44); Lockyer (*ibid.* 1899, 65, 449); Pollock and Leonard (*Sci. Proc. Roy. Dubl. Soc.* 1907, [ii.] 17, 217); Dufour (*Compt. rend.* 1908, 146, 810); De Gramont and de Watteville (*ibid.* 1908, 147, 239); Porlezza (*Gazz. chim. ital.* 1912, 42, ii. 42); Jevons (*Proc. Roy. Soc.* 1913, A, 89, 187); Crookes (*ibid.* 1914, A, 90, 512); McLennan

and Edwards (Phil. Mag. 1915, [vi.] 30, 482); Fowler (Proc. Roy. Soc. 1923). For its band spectrum, *v.* Porbezza (Gazz. chim. ital. 1923, 53, i. 215).

The refraction equivalent of silicon is 7.4 (Gladstone, Chem. Soc. Trans. 1891, 299).

For its refraction and dispersion in combination, *v.* Abati (Gazz. chim. ital. 1897, 27, ii. 437); Bygdén (Zeitsch. physikal. Chem. 1915, 90, 243). Sp.ht. 1.36 at -39.8° ; 2.029 at 232.4° (Weber, Ann. Chim. [5] viii. 132). Morphotropic relations between carbon and silicon compounds, *v.* Jerusalem (Chem. Soc. Trans. 1910, 2190).

For the specific heat of silicon and carbide of silicon at high temperatures, *see* A. Magnus (Ann. Physik. 1923, 22, 70, 303).

Estimation *v.* ANALYSIS.

Silica, silicic anhydride, SiO_2 , mol. formula $(\text{SiO}_2)_2$ (Schwarz and Sturm, Ber. 1914, 47, 1735), occurs abundantly in nature, in pure or nearly pure condition, the crystalline varieties including quartz, chalcedony, hornstone, jasper, tridymite, quartzite and lutecite, while in the amorphous state it is found in the various forms of opal. In impure condition it occurs as sand and flint, and it enters largely into the constitution of sandstones, felspars, and many other rocks. It occurs also in the feathers of birds in amount, apparently, dependent on the content of silica in the food. In the case of the dove, *Columba palumbus*, it forms 77 p.c. of the ash (Gonnermann, Zeitsch. physiol. Chem. 1918, 102, 78).

Silica may be artificially prepared:—

1. By burning silicon in air or oxygen.
2. By the action of water upon the tetrahalides of silicon, the gelatinous hydrate obtained yielding silica on ignition as a very light, white powder.
3. By the decomposition of silicates.

Many of these are decomposed by acids, and the silica so obtained from them often resembles the mineral from which it is derived. Chrysolite on boiling with dilute acids yields silica which is brilliantly white and fibrous like the mineral. Even after heating to redness it still retains the flexibility of silk. Serpentine and magnesian silicates generally, yield fibrous and not gelatinous silica (Terreil, Compt. rend. 100, 251; *v.* also Gorgeu, *ibid.* 98, 1281). A crystalline flourey form of silica has been observed to form on limestone. It is so finely divided that it passes through a filter and does not settle in water. Silicates which are not attacked by acids may be decomposed by fusion with sodium and potassium carbonates, the silica being rendered insoluble by subsequent evaporation with hydrochloric acid.

Properties.—The physical properties of natural silica vary somewhat with the different forms. Crystalline varieties have sp.gr. 2.3–2.8 (quartz=2.64–2.67; tridymite=2.28–2.43) and amorphous forms 1.9–2.3 (quartz glass, 2.213; Day and Shepherd, J. Amer. Chem. Soc. 1906, 28, 1089). Quartz (silver sand) when ground loses in density owing to its conversion into the vitreous variety. A sample of silver sand when unground of sp.gr. 2.638, when ground for 15 hours had its density reduced to 2.528, or 25.7 p.c. of the material was converted to the vitreous state. This is in conformity

with the fact that the molecular heat of solution of quartz (silver sand) after grinding for 15 hours was found to be 2.17 kgm.-calories higher than that observed in the case of material which had not been subject to grinding. The difference between the molecular heats of solution of quartz and vitreous silica is 6.95 kgm.-calories. So that in this case 31.2 p.c. of the material had been converted into the vitreous state by 15 hours' grinding (Ray, Roy. Soc. Proc. 1922, A, 101, 509, 102, 640). Other physical constants for the natural varieties will be found under the various minerals.

In presence of fused chlorides, quartz glass crystallises as quartz below 760° , and as tridymite above 800° , while at the lower temperature tridymite changes to quartz, the change being enantiomorphic (Day and Shepherd, *l.c.*). The crystalline forms can also be obtained artificially from solution (Chrustschoff, Jahrb. Min. 1887, 1 Mem. 205; Königsberger and Muller, Centr. Min. 1906, 657, 728).

Cristobalite is obtained by heating powdered transparent silica glass in a porcelain furnace. Sp.gr. 2.319, m.p. $1710^{\circ} \pm 10^{\circ}$. Tridymite (natural) melts at $1670^{\circ} \pm 10^{\circ}$.

Amorphous silica prepared by fusion in the electric furnace has a mean coefficient of expansion of 0.0000007 between 0° and 1000° (Le Chatelier, Compt. rend. 1900, 130, 1703).

Its m.p. is about 1600° . It can be quickly volatilised in an electric arc of 360 ampères and 70 volts, and in this way may be separated from zirconia or thoria (Moissan, Compt. rend. 116, 1428; *v.* also Cramer, Zeitsch. angew. Chem. 1892, 484; Schützenberger, Compt. rend. 116, 1230).

Quartz sublimes fairly readily in hydrogen at 1300° , but not in nitrogen (Wartenberg, Zeitsch. Elektrochem. 1912, 18, 658).

Silica is a catalyst of alcohols (Senderens, Compt. rend. 1908, 146, 125). With the moderately calcined substance, ethylenes are obtained almost exclusively, the yield from ethyl alcohol at 280° being 99.5 p.c.

Heat of formation 190.985 cal. (Mixer, Amer. J. Sci. 1907, [iv.] 24, 130).

For crystallography of polymorphous forms of silica, *see* Barlow and Pope (Chem. Soc. Trans. 1908, 1554). Silica is insoluble in microcosmic salt. It is slightly soluble in acids. Hydrofluoric acid decomposes it, forming water and silicon fluoride. The different modifications of silica reduced to a uniform fineness by electrification are very differently attacked by hydrofluoric acid, amorphous silica being dissolved 10 times faster than quartz, which is the least reactive of all the forms of silica. It dissolves fairly readily in caustic soda, hyalite dissolving more slowly than the other varieties; quartz requires boiling or increased pressure. Amorphous silica in fine powder and gelatinous silica dissolve partially in alkali carbonate solutions, the silica being deposited in gelatinous form on cooling. It is readily converted into alkali silicate by fusion with alkali hydroxide or carbonate. It is slightly soluble in water, and is distinctly hygroscopic, this property decreasing with the degree of calcination (Souchy, Bull. Soc. chim. [2] 13, 509). At 25° the solubility figures after digesting for 2 days were: water 0.0032 grm.; 6.4 p.c. HCl 0.0044; 34.9 p.c. HCl

0.004 grm. per 50 c.c. At 90° the solubility of gelatinous silica per 50 c.c. is 0.0212–0.0216 grm. in water; 0.024 grm. in 1.2 p.c. HCl; 0.0028 in 18.7 p.c. HCl; 0.0211 in 3.9 p.c. H₂SO₄; and 0.0004 in 71 p.c. H₂SO₄ (Lenher and Merrill, J. Amer. Chem. Soc. 1917, 39, 2630; 1921, 43, 391).

With PCl₃ and PCl₅ at red heat, SiCl₄ is produced, as is the case when chlorine is passed over a mixture of the oxide with charcoal at red heat. It is not affected, however, by CCl₄.

It is reduced by metals (*v. Silicon, Preparation of*), and by carbon in the electric furnace (Moissan, Compt. rend. 1895, 120, 1393). For its action upon alkaline haloid salts, *v. Gorgeu* (Compt. rend. 102, 1164).

It gradually absorbs lime from lime-water, forming 3SiO₂·4CaO (Laudrin, *ibid.* 96, 841). Kieselguhr shaken with lime-water swells by absorption of lime, but there is no formation of silicate; the phenomenon is purely physical. It is dissolved in small quantities by ammonia (Souchay, Zeitsch. anal. Chem. 1872, 182). Its use has been advocated for decolorising oils (Stern, Warsaw, Eng. Pat. 1890, 7142). While not an essential constituent of plant food it plays a definite part in the nutrition of cereals (Hall and Morison, Proc. Roy. Soc. 1906, 77 B, 455).

The velocity of transformation of one form of silica into another is extremely slow, and the different forms may exist together over considerable ranges of temperature. The inversions may be hastened by employing a catalytic agent (sodium tungstate).

α -quartz (tetrahedral hexagonal) \rightleftharpoons β -quartz (hemihedral hexagonal) 575°.

β -quartz \rightleftharpoons β -tridymite (holohedral hexagonal) 870°±10°.

β -tridymite \rightleftharpoons β -cristobalite (cubic) 1470°±10°.

On cooling, β -tridymite and β -cristobalite promptly pass at the following temperatures into metastable forms possessing lower optical symmetry:—

β -tridymite \rightleftharpoons α -tridymite (biaxial, perhaps orthorhombic) 115°–120°.

β -cristobalite \rightleftharpoons α -cristobalite (biaxial) 180°–270°.

(Fenner, J. Washington Acad. Sci. 1912, 2, 471; *cf.* Endell and Rieke, Zeitsch. anorg. Chem. 1912, 79, 239; Smits and Endell, *ibid.* 1913, 80, 176; *idem.* 1919, 106, 143; Michie, Chem. Zeit. 1913, 37, 589; Ferguson and Merwin, Amer. J. Sci. 1918, 46, 417; Fenner, J. Soc. Glass Tech. 1919, 3, 116.)

For the crystal structure of quartz, *see* L. W. McKeehan (Physical. Rev. 1923, 21 503–508; J. Chem. Soc. 1923, 123, 124, ii. 633). For the scattering of light by smoky quartz, *see* Sur (Indian Assoc. for Cultivation of Sci. Proc. 8, 4, 271, 1923; Sci. Abstr. 1924, 27, 792).

Fused silica-ware is now extensively employed in laboratory and technological operations. The first attempts to utilise silica in this way were made by Gaudin in 1839 (Compt. rend. 8, 678, 711), who succeeded in spinning threads of fused silica by hand, and also made small pellets which he found to be inactive to polarised light. The production of capillary tubes and spirals was described by Gautier in

1869 and exhibited at the Paris Exhibition in 1878. In 1887, Boys (Phil. Mag. 1887, 489) produced quartz fibres, the torsion of which he applied to the measurement of small forces; he also produced small tubes and bulbs. Other early workers were Dufur and Le Chatelier, and the firm of Schott and Genossen, in Jena, who exhibited a quartz lens in the Paris exhibition of 1900. In 1901, Shenstone (Proc. Roy. Inst. 1901, 525) demonstrated a method of producing before the oxy-coal-gas blowpipe flame, tubes, bulbs, and other apparatus suitable for use in scientific work.

In 1903 Heraeus, of Hanau, described a method of fusing quartz and exhibited a number of articles made of it by Siebert and Kuhn of Cassel.

Physical properties.—Sp.gr. 2.21 (*v.* Day and Shepherd, *l.c.*). Coefficient of expansion 44.9×10^{-8} (Minchin, Phys. Review, 1907; *v.* also Le Chatelier, *l.c.*; Kaye, Phil. Mag. 1910, 20, 718). Harlow (Proc. Phys. Soc. 1911, 24, 30) found for the interval 0°–100° the cubical expansion as 99.8×10^{-8} , and for 0°–184° as 144.7×10^{-8} . It expands on cooling from 1500° to 1200° (Le Chatelier, *l.c.*). Refractive index for D line 1.4584772 (Shenstone and Gifford, Proc. Roy. Soc. 1904, 201). Specific heat $0.1685 + 0.000194\theta - 0.00000011\theta^2$.

Its m.p. is not well defined; at the m.p. of platinum it is appreciably soft, but not workable. It probably commences to soften at about 1500°. It vaporises freely in the electric arc, but at its b.p. is still a very viscous liquid, nor does its fluidity increase on raising the b.p. by increasing the pressure.

In consequence of its low coefficient of expansion it possesses to a remarkable degree the power of resisting sudden changes of temperature. Vessels made of it may be heated to redness and immersed in cold water without cracking. Boys has shown it to be an excellent insulator, even in an atmosphere saturated with moisture. Its specific inductive capacity is 3.5–3.6.

Silica glass is permeable to hydrogen at high temperatures and pressures. The permeability is proportional to the gas pressure and is an exponential function of the temperature. The transfusion begins at the temperature at which structural changes occur. It becomes appreciable at 300°. It is also permeable to helium, and the permeability is easily measured at 182°. At 500° the permeability for helium is 22 times that of hydrogen. Neither pyrex glass nor Jena combustion tubing are permeable to hydrogen. At 610° pyrex glass is permeable for helium (Williams and Ferguson, J. Amer. Chem. Soc. 1922, 44, 2160; Villard, Compt. rend. 130, 1752; Berthelot, *ibid.* 140, 821).

PHYSICAL PROPERTIES OF QUARTZ FIBRES.

Diam. of thread	0.00175 cm.	tenacity	8.0×10^9 C.G.S.
"	0.00048 "	"	11.5×10^9 "
Young's modulus at 20°C.	"	"	5.6×10^9 "
Modulus of simple rigidity at 20°C.	"	"	2.65×10^9 "
" incompressibility	"	"	1.4×10^9 "
" torsion	"	"	3.7×10^9 "

(Threlfall, Laboratory Arts, 218).

The mean expansion coefficient of quartz parallel to the axis between 0° and t° is given by the expression $(7.158 + 0.00816t)$ (Nakamura, Science Abstracts, 1918, 376).

Chemical properties.—Fused silica is very resistant, being attacked only by fused alkalis, hydrofluoric acid, and to a small extent by phosphoric acid. Even with hydrofluoric acid no etching is produced if the silica be pure, the material dissolving away so as to leave a smooth surface. Certain metallic oxides, such as those of lead and copper, attack silica if heated in contact with it.

Fused silica, on account of its slow devitrification, due to its tendency to revert to cristobalite and later to tridymite, which commences at 1200°, should not be used for continuous work at higher temperatures, though quite satisfactory for intermittent work, *i.e.* pyrometric measurements. It is used as a standard of length at the National Physical Laboratory (Kaye, Proc. Roy. Soc. 1911, A, 85, 430) and in mercurial thermometry. Fused silica has been adopted as material for beakers, and basins for the concentration of sulphuric acid, for gutters and lips for Glover towers, for pipes, coolers, &c. Silica is better than porcelain for electric resistance furnaces wound with platinum foil, as there is no appreciable action on the platinum. A silica tube which has been repeatedly quenched from 1000° gradually becomes porous so that a vacuum cannot be maintained in it. Silica tubes can be bent and worked at temperatures above 1500°.

Fused silica ware (known as vitreosil) is now largely employed as an acid-proof material in chemical manufacturing. For a description of its manufacture and properties, see Bottomley, J. Soc. Chem. Ind. 1917, 36, 577. For information as to the refractory properties of silica and silica wicks, see Le Chatelier and Bogitch, Compt. rend. 1917, 165, 218; Le Chatelier, Rev. Mét. 1917, 14, 74.

Silica finds further commercial application in the manufacture of artificial stone and hydraulic cements. Kieselguhr is employed in making dynamite, ultramarine, water-glass enamels and glazes, also as a polishing agent, a filling material for paper, soap, and other articles, and as a medium in the filtration of water (*v.* Nordtmeyer, Chem. Zentr. 1891, 932).

According to P. B. Robinson and W. J. Rees (Trans. Ceram. Soc. 1923–24, 23, 1), results of screening and other tests on green silica bricks were correlated with results obtained from the corresponding burned brick, with the object of determining the type of rock and grading which will produce a mechanically strong silica brick. The necessity for using a hard fine-grained rock crushing into fragments of high angularity is emphasised. The grinding should be of such duration that the brick will contain about 40 p.c. of material retarded by a 30-mesh to the inch sieve, and about 40 p.c. which will pass through a sieve of 90 meshes per inch. Burning to cone 20 (1530°) considerably increases the mechanical strength of the brick (J. Soc. Chem. Ind. 1924, 43, B. 513).

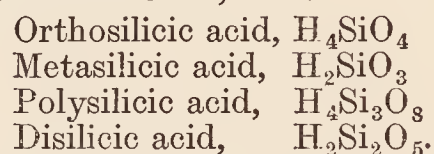
MANUFACTURE OF SILICATES OF BASIC DYE-STUFFS.

Lake colours containing up to 20–80 p.c. of basic dyestuffs can be prepared by heating a base-exchanging silicate with the dyestuff and

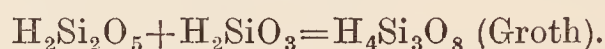
with a quantity of water insufficient to dissolve the latter. An alkali and a protective colloid may be added with advantage. For example, 5 kgs. of methylene blue are ground with about 5 kgs. of a base-exchanging zeolite, and the mixture is boiled with about 5 litres of water until complete fixing of the dyestuff takes place. A larger proportion of dyestuff may be fixed by heating under increased pressure (W. Eberlein, Eng. Pat. 201941, 1923, conv. 1922; J. Soc. Chem. Ind. 1924, 43, B. 526).

Silicon monoxide SiO is described by Potter (D. R. P. 189833) as a voluminous brown powder obtained by heating silica electrically in an inert atmosphere with sufficient carbon or carbon silicide to remove one half of the oxygen; sp.gr. 2.24. Much less readily soluble in hydrofluoric acid than silica, but more readily soluble in potassium hydroxide. It is patented as a pigment under the name of 'monox' (Eng. Pat. 1279, 1906).

Silicic acids. Four silicic acids are usually stated to exist, viz.:



Polysilicic acid may be regarded as composed of metasilicic and disilicic acids:



On the other hand, orthosilicic acid and polysilicic acids may combine together to form metasilicic acid: $\text{H}_4\text{SiO}_4 + \text{H}_4\text{Si}_3\text{O}_8 = 4\text{H}_2\text{SiO}_3$; and disilicic acid may be regarded as polysilicic acid from which orthosilicic acid has been abstracted: $3\text{H}_4\text{Si}_3\text{O}_8 - \text{H}_4\text{SiO}_4 = 4\text{H}_2\text{Si}_2\text{O}_5$ (Becker Am. S. 38, 154).

Considerable difference of opinion still exists as to the actual existence of definite hydrates of silica, Chatelier (Compt. rend. 1908, 147, 660) holding that the water is not chemically combined. The existence of *metasilicic acid* H_2SiO_3 would, however, appear to be proved. According to Butureanu (Ann. Sci. Univ. Jassy, 1901, 1, 319) it is obtained as a white powder by dehydrating gelatinous silicic acid, prepared by adding mineral acid to an alkali silicate solution, with 90 p.c. alcohol.

Orthosilicic acid H_4SiO_4 is said to be obtained by washing the precipitated silicic acid prepared by the action of silicon fluoride upon water, with benzene or ether, and rapidly drying between bibulous paper (Norton and Roth, J. Amer. Chem. Soc. 1897, 19, 832) and also by the action of silicon chloride upon water (Tschermak, Zeitsch. anorg. Chem. 1909, 63, 230).

According to Schwarz and Liede (Ber. 1920, 53, 1680), by leading silicon fluoride into boiling water a form of silicic acid is obtained which dissolves less readily in hydrofluoric acid, or in sodium hydroxide or ammonia solution, than the normal α -acid or ortho-acid. It is termed β -acid. Conductivity experiments on its solution in ammonia indicate that it is a more highly polymerised form, analogous in some respects to metastannic acid.

Tschermak, in the course of his work upon the constitution of silicates, claims to have proved the existence of other hydrates, by the breaks in the dehydration curves of the gels obtained by decomposing the silicates with

hydrochloric acid. His conclusions are based on the assumption that the acid set free is the acid from which the salt is formed, and that the process of drying takes place in two distinct stages—evaporation of excess of water, followed by dehydration of the acid (Centr. Min. 1908, 129, 225; Zeitsch. anorg. Chem. 1910, 66, 199). The method is adversely criticised by Mügge (Centr. Min. 1908, 129, 325), van Bemmelen (Zeitsch. anorg. Chem. 1908, 59, 225; 1909, 62, 1), and Serra (Atti R. Accad. Lincei, 1910, [v.] 19, 1, 202). The last-named finds that the temperature and concentration of the hydrochloric acid, and the temperature at which the silicic acid is dried, influence the result.

The various hydrates described by Merz (J. pr. Chem. 99, 177), Gottlieb (*ibid.* [2] 6, 185), and Langlois (Chem. Soc. Trans. 1858, 140) are probably not definite compounds (Carnelly and Walker, *ibid.* 1888, 1, 66, 80). Cf. Lenher, J. Amer. Chem. Soc. 1921, 43, 391.

Gelatinous silica (hydrogel form) is also obtained by the action upon alkali silicate solutions of oxalic (Monier, Compt. rend. 86, 1318), sulphurous (Doveri, J. pr. Chem. 42, 194), carbonic, and boric acids (Vogel, Jahresber. 1870, 295), and a large number of other acids (Holmes, J. Phys. Chem. 1918, 22, 510), and the physical properties vary with the conditions of precipitation, particularly its solubility in water. According to Jordis (Zeitsch. Electrochem. 1905, 11, 835; Chem. Zentr. 1907, 1, 392), the hydrogel produced with sodium silicate and hydrochloric acid may be soaked in water until finally neither hydrogel nor washings give a reaction for chlorine. If then extracted with hot water the washings again give a strong reaction for chlorine. Sodium is also present, and Jordis considers that these elements are not present in the form of sodium chloride.

For conditions necessary to produce a gel which will set in a definite time, see Holmes, *l.c.*

For the ultramicroscopic study of silicic gels, v. Zsigmondy (Zeitsch. anorg. Chem. 1911, 71, 356).

For an account of the properties of hydrated silica of various degrees of hydration, prepared from silica gel, see Berl and Urbain (Zeitsch. angew. Chem. 1923, 36, 57).

For silica gel as an industrial adsorbent, see E. C. Williams (J. Soc. Chem. Ind. 1924, 43, 97, T).

Silicic acid is a very weak acid. In its colloidal form it may be detected by its solubility in boiling alkali paratungstate solutions, forming silico-tungstates. The potassium salt in presence of sodium chloride gives a crystalline precipitate with 5 p.c. caesium chloride solution (Hermann, Zeitsch. anal. Chem. 1907, 46, 318). Silica jelly is an excellent culture medium for micro-organisms (Kühne, Zeitsch. Biol. 27, 172). It also finds application in sugar refining (Vibrans, Chem. Zeit. 1880, 426).

Soluble silicic acid (hydrosol) was the subject of researches by Graham, upon the results of which he laid the foundations of colloid chemistry. If a dilute solution of an alkali silicate be poured into large excess of hydrochloric acid, the silicic acid remains in solution, and may be purified by dialysis by means of parchment paper, and concentrated by evapora-

tion to a silicic acid content of 18 p.c. The solution is tasteless and limpid, with a slightly acid reaction, and readily coagulates. Hydrochloric acid and small quantities of potash or soda retard the coagulation. Evaporated at 15° *in vacuo* the silica remains as a transparent glassy, lustrous hydrate containing 22 p.c. of water (Chem. Soc. Trans. 1861, 204; v. also Church, J. pr. Chem. 89, 187; Doveri, *l.c.*; Kühn, J. pr. Chem. 59, 1).

It may also be obtained by hydrolysis of methyl silicate (8 grms.) with water (200 grms.) at boiling temperature, and evaporating to two-thirds its bulk to expel methyl alcohol, the solution so obtained containing 2.26 p.c. of SiO_2 , and differing from Graham's solution in that it is not coagulated by carbon dioxide (Grimaux, Compt. rend. 98, 1434).

Electrolysis of a 1.5 p.c. solution of water-glass between a mercury cathode and a platinum anode in a Hildebrand cell produces a clear hydrosol of silicic acid which does not gelatinise for weeks. The sol from a 6 p.c. solution gelatinises immediately it is formed, and a 30 p.c. solution deposits silica on the anode (Kröger, Kolloid-Zeitsch. 1922, 30, 16).

The coagulating effect of electrolytes has been studied by Pappada and Sadowski (Zeitsch. Chem. Ind. Kolloide, 1910, 6, 292), who find the effects of different ions to be approximately proportional to their rates of diffusion.

Dialysed silicic acid containing the least trace of hydrochloric acid gives no luminous beam when optically examined, even on evaporation, showing that the molecular aggregates are not sufficiently large to scatter light. If completely dialysed, the gradual condensation is indicated by a feebly luminous beam, slowly increasing in intensity (Picton and Linder, Chem. Soc. Trans. 1892, 154).

Mylius and Groschuff (Ber. 1906, 39, 116) find the molecular weight of soluble silica when freshly prepared (α -silicic acid) to be about 155. It is not precipitated by egg-albumen, methylene blue, or sodium hydroxide, but slowly changes—rapidly on warming—to the β -silicic acid, which is also soluble, but is precipitated by these substances, and according to Sabanéeff (J. Russ. Phys. Chem. Soc. 21, 515) has a molecular weight of not less than 48,000. Heat of coagulation +11.8 cal. (Wiedemann and Lüdeking, Ann. Chim. [2] 25, 145).

Alkosol and alkogel, and corresponding glycerol compounds with silicic acid, are also described by Graham (J. pr. Chem. 94, 347).

Esters corresponding to the acids, H_2SiO_3 and H_4SiO_4 , are also known.

For the demonstration of the phosphorescence of fused transparent silica, see Curtis (Phys. Soc. of London Proceedings, 1924, 36, Aug. 431).

ORTHOSILICIC ACID IN PORTLAND CEMENT.

Additional experiments have confirmed F. Hart's (Zement, 1924, 13, 78) previous conclusion (B. 1924, 296), that orthosilicic acid is present in Portland cement. The dehydration curve of the gel from a sample of 'dusting' cement showed one break at 35.69 p.c. of water, and a second at 31.27 p.c. of water, indicating

the presence of two different silicic acids, viz. orthosilicic acid and $2\text{SiO}_2, 3\text{H}_2\text{O}$, the latter being formed by the removal of one molecule of water from two molecules of $\text{Si}(\text{OH})_4$. The dehydration curve of the gel obtained from that part of the dusting cement which consisted of particles remaining on a 5000-mesh (per sq. cm.) sieve showed a break at 37.9 p.c. of water, corresponding to orthosilicic acid and to a normal Portland cement, but that of the finer portion of the cement showed two breaks, one at 37.7 p.c. of water, and the second at 33.1 p.c., corresponding to orthosilicic acid and to $2\text{SiO}_2, 3\text{H}_2\text{O}$ respectively. This confirms the widely accepted opinion that 'dusting' is due to the presence of a silicate which is deficient in lime. Another cement of low tensile strength yielded a gel, the dehydration curve of which showed a break only at 32.8 p.c. of water, indicating that only a small proportion of orthosilicic acid was present, together with a large proportion of $2\text{SiO}_2, 3\text{H}_2\text{O}$. A blast-furnace cement was found, in the same way, to contain orthosilicic acid, but the gel was unusually voluminous when first formed, and on drying to the critical point (36.7 p.c. water) consisted of small crusty fragments of horn-like material, whereas the dried gel from normal cement forms a soft white powder (J. Soc. Chem. Ind. 1924, 43, B. 516).

The conversion, in aqueous solution, of colloidal into non-colloidal silica is effected by dissolved salts and is accelerated by rise of temperature, alkali carbonates aiding the conversion to a greater extent than neutral salts, whilst salts with an acidic reaction (e.g. aluminium sulphate) hinder the change. The latter is so much more rapid in quartz than in platinum vessels that in the former case it proceeds quickly in absence of salts, which are essential when platinum vessels are used. The dialysis of a solution obtained by mixing sodium silicate and hydrochloric acid solutions has been followed by the molybdate method. A solution of sodium (or potassium) silicate was kept for several months. On passing through it a current of carbon dioxide an increase in the amount of silica (as measured by the molybdate method) was observed, the original silica content being restored, however, 24 hours later, when the carbon dioxide had disappeared (F. Diénert and F. Wandenbuleke, Compt. rend. 1924, 178, 564; J. Soc. Chem. Ind. 1924, 43, 254).

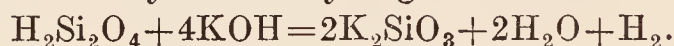
Thiosilicic acid is only known in the form of its sodium salt, which is obtained by fusing together pure sodium sulphide and silicon disulphide. Na_2SiS_3 is a brownish-black mass decomposed by water and acids (Hempel and Haasy, Zeitsch. anorg. Chem. 1900, 23, 32).

COMPLEX ACIDS CONTAINING SILICON.

The chief of these are *silico-stannic*, *silico-titanic* (Bourgeois, Compt. rend. 104, 231), *silico-zirconic* (Ouvrard, *ibid.* 113, 82), *silico-molybdic* (Asch. Zeitsch. anorg. Chem. 1901, 28, 273; Copaux, Ann. Chim. 1906, [viii.] 7, 118; Bull. Soc. franc. Min. 1907, 30, 292; Mélikoff, Compt. rend. 1912, 154, 1478; Rosenheim and Jaenicke, Zeitsch. anorg. Chem. 1917, 101), *nitro-silicic* (Rousseau and Tite, Compt. rend. 114, 294), and *silico-tungstic* (Copaux, Bull. Soc.

chim. 1908, [iv.] 3, 101; Rosenheim and Jaenicke, *l.c.*). Sodium silico-tungstate is a good mordant for basic aniline colours (Scheurer, Leipziger Farber- und Lendgr. Zeit. 1900, 49, [6] 60). The free acid or its sodium salt in 5 p.c. solution is said to be the best general precipitant for alkaloids, forming precipitates which are practically insoluble in cold water, and from which the alkaloid is at once regenerated by dilute soda or ammonia (Bertrand, Compt. rend. 1899, 128, 742; Javillier, Chem. Zentr. 1912, ii. 36; Taigner, Zeitsch. anal. Chem. 1919, 58, 346; Heiduschka and Wolff, Schweiz. Apoth. Zeit. 1920, 58, 213-329).

Silico-oxalic acid $\text{O} : \text{SiH} \cdot \text{O} \cdot \text{O} \cdot \text{SiH} : \text{O}$ or $\text{O} : \text{Si}(\text{OH}) \cdot \text{Si}(\text{OH}) : \text{O}$ is a white solid obtained by exposing pure Si_2Cl_6 in a platinum dish cooled in ice, till solid, and then over lime until all hydrochloric acid is removed. By treating hexaethylsilicoethane $\text{Si}_2(\text{OEt})_6$ by water in the cold; $\text{Si}_2(\text{OEt})_6 + 4\text{H}_2\text{O} = \text{Si}_2\text{O}_4\text{H}_2 + 6\text{EtOH}$. When heated in a test-tube it decomposes violently with feeble detonation, and also explodes with friction or pressure. With potassium hydroxide hydrogen is evolved



It reduces KMnO_4 in the cold (Friedel and Ladenburg, Annalen, 203, 250; Gatterman and Weinlig, Ber. 27, 1943; v. also Troost and Hautefeuille, J. pr. Chem. [2] 4, 302).

Silico-mesoxalic acid



is similarly obtained from Si_3Cl_8 , but is more violently explosive, and has stronger reducing properties than the silico-oxalic acid. When dry it is extremely unstable, often decomposing spontaneously and becoming incandescent (Gattermann and Ellery, Ber. 32, 1114).

Silico-formic anhydride (dioxodisiloxane)

$\text{O} : \text{SiH} \cdot \text{O} \cdot \text{SiH} : \text{O}$ (v. under SILICO-CHLOROFORM).

Silicones. These oxygen-hydrogen compounds of silicon are produced by the action of aqueous hydrochloric acid on metallic silicides.

Chryseone or *silicone* $\text{Si}_4\text{H}_4\text{O}_3$ is described by Wöhler as obtained in orange-coloured laminae by digesting calcium silicide with concentrated hydrochloric acid in absence of light. On exposure it becomes snow-white in colour, changing to *leucone* $\text{Si}_3\text{H}_4\text{O}_5$. If dilute acid is used, the substance, $\text{Si}_4\text{H}_8\text{O}_5$, is obtained (Wöhler and Buff, Annalen, 104, 101; Wöhler, *ibid.* 127, 257). Hönigschmidt (Monatsh. 1909, 30, 509) assigns to silicone the formula $\text{Si}_3\text{H}_2\text{O}_2$ from the amount of hydrogen evolved when heated in a vacuum. The residue has the composition Si_3O_2 . Leucone gives no definite result by this method, but leaves a residue approximating in composition to Si_3O_4 . Similar compounds of indefinite composition are obtained from magnesium and other silicides (Geuther, J. pr. Chem. 95, 424; Winckler, Ber. 23, 2642). They are probably mixtures of silicoformic anhydride and silico-oxalic acid (Boudouard, Compt. rend. 1906, 142, 1528).

SILICON AND HYDROGEN.

Silicon hydride, *silicomethane*, *monosilane*, SiH_4 , was first obtained, mixed with hydrogen, by Wöhler and Buff (Annalen, 102, 128; 103, 218; 104, 94; 107, 112; Jahresber. 1857, 166;

1858, 142), (a) by electrolysis of sodium or other metallic chloride using as the positive pole an alloy of aluminium and silicon, at which the spontaneously inflammable gas escapes; (b) by the action of hydrochloric acid on magnesium silicide and other silicides.

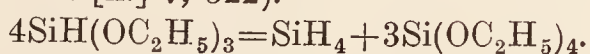
So obtained by Wöhler and Buff it is a colourless, spontaneously inflammable gas, insoluble in de-aërated water, but decomposed over water containing air. SiH_4 may be obtained by direct synthesis from its elements. Silicon heated above its melting-point in hydrogen yields small quantities of SiH_4 (Dufour, Ann. Chim. 1906, [viii.] 9, 433).

The crude gas from magnesium silicide usually consists of about 95 p.c. hydrogen. During the preparation a white solid forms in amount equal to 25–30 p.c. of the magnesium silicide used. It is *silico-oxalic acid* $\text{Si}_2\text{O}_4\text{H}_2$ (Besson, Compt. rend. 1912, 154, 1603). On fractionating the gas by means of liquid air, Moissan and Smiles obtained a fraction boiling at about 52° , spontaneously inflammable, and of density approximately agreeing with the formula Si_2H_6 (Compt. rend. 1902, 134, 569).

Subsequently, Lebeau (*ibid.* 1909, 148, 13) obtained by this method SiH_4 and Si_2H_6 in the pure state, the latter of the calculated density and of b.p. -7° , and in addition a colourless liquid exploding violently with oxygen, and burning with a bright flame. This is probably Si_2H_4 , although too reactive to allow of accurate analysis, and is probably the cause of the spontaneous inflammability of the crude gas.

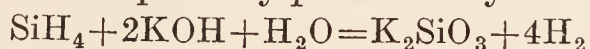
The production of silicon hydrides by this method has been studied by Stock and Somieski (Ber. 1916, 49, 111), who have described a convenient method of preparing the magnesium silicide and of effecting its decomposition by hydrochloric acid.

Silico-methane is obtained in the pure state by the decomposition on warming of tri-ethyl silico-ortho-formate in contact with sodium. The action of the sodium has not been explained (Friedel and Ladenburg, Bull. Soc. chim. [ii.] 7, 322).



According to Adwentowski and Drozdowski (Bull. Acad. Sci. Cracow, 1911, A, 330–344) this method only yields the pure gas after repeated fractionation. It is not spontaneously inflammable, except when gently heated under reduced pressure, or mixed with hydrogen. A hot knife-blade is sufficient to inflame the bubbles of gas as they rise over mercury, until the mercury becomes sufficiently heated to set fire to the succeeding bubbles. Its heat of formation is about 9000 calories (Wartenberg, Zeitsch. Elektrochem. 1912, 18, 658).

It is decomposed by potassium hydroxide



1 litre at N.T.P. weighs 1.4538 grams; crit. temp. -35°C .; crit. press. 47.8 atmos.; b.p. $-116^\circ/740$ mm. (Adwentowski and Drozdowski, *l.c.*); m.p. -185° ; b.p. $-112^\circ/760$ mm. $D_{-185}^{25} 0.68$ (Stock and Somieski). Heat of formation 24.8 cal. (Ogier, Compt. rend. 88, 911). Heat of combustion 324.3 cal.

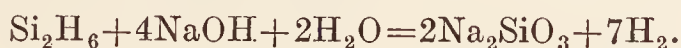
The gas has a faint but characteristic odour, recalling stibine; it is very stable at the ordinary

temperature; its spontaneous inflammation in the air is uncertain, small bubbles as a rule failing to fire; when containing other hydrides of silicon it inflames invariably. Reacts with hydrogen bromide in presence of aluminium bromide to give SiH_3Br and SiH_2Br_2 ; with hydrogen chloride in presence of aluminium chloride yields chloromonosilane; m.p. -118° , b.p. -30.5° .

It forms with copper and silver solutions the corresponding silicide, and precipitates metallic palladium from solution, but is without action on lead acetate or platinum chloride. It is decomposed by the electric discharge into hydrogen and a yellow solid (Ogier, Compt. rend. 89, 1068).

Stock, Stiebeler and Zeidler have investigated the composition and properties of the less volatile silicon hydrides obtained by the action of acid on magnesium silicide. The liquid products were fractionally distilled in a vacuum and the fractions of the distillate collected at temperatures from -185° upwards. A yellow, amorphous, solid residue was obtained which, from its analysis and its behaviour towards bromine, appeared to be a polymeride of silicon monohydride $[\text{SiH}]_x$. The following physical measurements were made: *silicopropane* Si_3H_8 , $d_4^{20} 0.743$, m.p. -117.4° , b.p. 53° ; *silicobutane* Si_4H_{10} , $d_4^{20} 0.825$, m.p. about -90° , b.p. 109° . The higher members of the series are less stable to light and appear to decompose according to the scheme $\text{Si}_5\text{H}_{12} \rightarrow 2[\text{SiH}]_x + \text{Si}_2\text{H}_6 + \text{SiH}_4$. This unsaturated hydride apparently cannot be obtained in a volatile form of low molecular weight. Whether obtained by the auto-decomposition of the silicoparaffins, by the action of the silent electric discharge on these compounds, by the action of acids on silicides, or by the action of sodium amalgam on silicoparaffins and their chlorides, it always appears in the solid, yellow, associated form, its composition varying between $[\text{SiH}]_x$ and $[\text{SiH}_{1.6}]_x$ (Alfred Stock, Paul Stiebeler and Friedrich Zeidler, Ber. 1923, 56, [B] 1695–1705; J. Chem. Soc. 1923, 123, 124, ii. 633).

Disilane Si_2H_6 melts at -132.5° , $D_{-25}^{25} 0.686$, b.p. $-15^\circ/760$ mm. A colourless gas of rather stronger odour than silane; can be preserved unaltered at ordinary temperatures, but decomposes rapidly at 300° . The gas invariably inflames in the air, sometimes with violent explosion. Like silane, it is decomposed by alkali hydroxide solutions, giving hydrogen and silica or alkali silicate:



Very soluble in benzene or carbon disulphide; the latter solution is extremely inflammable on access of air, frequently with explosion. Disilane at 500° suffers decomposition, analogous to the cracking of hydrocarbons, producing silicon, hydrogen, and monosilane. Monochlorosilane and hydrogen sulphide at 150° in presence of aluminium chloride yield hydrogen, dichloromonosilane, and a volatile compound containing sulphur, possibly $\text{SiH}_2\cdot\text{HS}$ or $(\text{SiH}_3)_2\text{S}$. Dichloromonosilane reacts with sodium amalgam to give monosilane and the unsaturated yellow polymerised hydride $(\text{SiH})_x$ (A Stock and G. Somieski, Ber. 1923, 56, [B.] 247; Chem. Soc. Absts. 1923, ii. 160). For halogen deriva.

tives, *v.* Stock and Somieski, Ber. 1920, 53, [B] 759.

Trisilane Si_3H_8 when cooled in liquid air forms a crystalline solid, m.p. -117° ; the liquid has D_0° 0.725, b.p. $53^\circ/760$ mm. A mobile colourless liquid, much less stable than silane and disilane, decomposing slowly at the ordinary temperature. Decomposed rapidly by alkaline solutions.

Tetrasilane Si_4H_{10} , a colourless liquid, D_0° 0.79, m.p. -93.5° , b.p. $80^\circ\text{--}90^\circ/760$ mm. Resembles trisilane in general properties. Decomposes fairly rapidly at ordinary temperatures. **Pentasilane** Si_5H_{12} and **hexasilane** Si_6H_{14} are also among the gases and resemble their lower homologues in their behaviour when heated and towards air, water, and alkali.

The quantities in which the several hydrides are present in the product of the action of hydrochloric acid on magnesium silicide decrease with increasing molecular weight of the hydrides. About one-fourth of the silicon present in the magnesium silicide is obtained in the form of silicon hydrides, the remainder being converted into silico-oxalic acid (Stock and Somieski, *l.c.*). Cf. Stock and Somieski, Ber. 1921, 54, [B] 524.

Trichloromonosilane, prepared from copper silicide and hydrogen chloride at 300° , and purified by fractional distillation in a vacuum, has m.p. -126.5° , b.p. 31.8° , d_0° 1.35. It is remarkably stable to heat and is unaffected by aluminium chloride at 175° ; at 900° it decomposes almost quantitatively into silicon, hydrogen, hydrogen chloride, and silicon tetrachloride. It is immediately decomposed by water, yielding solid non-volatile silicoformic anhydride, $[\text{HSiO}]_2\text{O}$; it reacts with sodium amalgam readily, probably according to the scheme $x\text{SiHCl}_3 + 3x\text{Na} \rightarrow 3x\text{NaCl} + (\text{SiH})_x$; and with ammonia, in the gaseous phase at low pressures or in the liquid state at low temperatures, it forms an imide



which decomposes on heating to yield mainly ammonia and SiHN (A Stock and F. Zeidler, Ber. 1923, 56, [B] 986; Chem. Soc. Absts. 1923, 124, ii. 412).

SILICON AND FLUORINE.

Silicon fluoride SiF_4 was first obtained by Scheele in 1771. It is produced by the action of hydrofluoric acid or concentrated sulphuric acid and a metallic fluoride, upon silica or silicates. Further, by strongly heating fluor-spar with silica, or a mixture of clay and carbon as well as by direct synthesis (*v.* also under SiHF_3).

It is most conveniently prepared by treating a mixture of one part fine dry sand or glass powder and one part powdered fluor-spar with six parts concentrated sulphuric acid, the gas being collected over mercury.

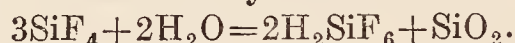
It is a colourless gas with a suffocating smell, and fumes strongly in air. It is not inflammable. It solidifies at -102° (Olzewski, Monatsh. 5, 127) and evaporates without fusion. Under two atmospheres pressure it solidifies without liquefying at -97° , and then melts at -77° , and boils at -65° under 1810 mm. Its critical temperature is -1.5° and its critical pressure

50 atmospheres. These constants are identical for both the synthetic product, and that obtained by the usual method (Moissan, Compt. rend. 1904, 139, 711). A normal litre weighs 4.6840 grms. (Germann and Booth, J. Phys. Chem. 1917, 21, 81).

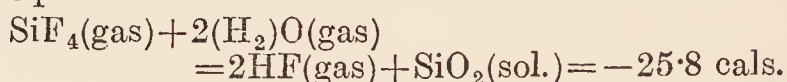
Its spectrum contains characteristic blue bands which are absent from the silicon hydride spectrum (Wesendonck, Wied. Ann. 21, 427; *v.* also Dufour, Compt. rend. 1908, 146, 810).

It is decomposed by continued passage of the electric spark, with separation of silicon (Troost and Hautefeuille, Compt. rend. 73, 443).

It is readily absorbed in large quantities by water, being at the same time partially decomposed into silicic and hydrofluosilicic acids



The solution always contains undecomposed silicon fluoride. It is not, however, decomposed by steam above 150° (Hautefeuille), and Guntz (Ann. Chim. [vi.] 3, 1) shows from the thermal equation



that the latter action can only take place provided the temperature is sufficiently high to prevent the secondary action, viz. combination of hydrofluoric acid with water and formation of hydrofluosilicic acid, which develops heat sufficient to compensate this absorption.

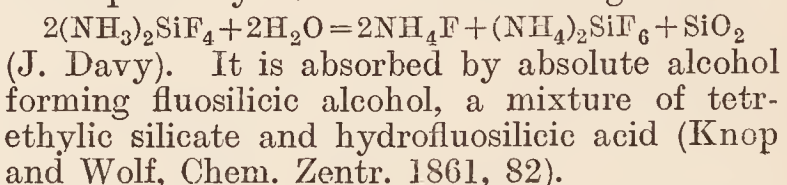
The heat of formation of silicon fluoride is 269.4 cal.

Aqueous alkalis and alkaline earths decompose it, precipitating part of the silica and forming a fluosilicate of the metal, as is the case with potash, or precipitating the whole of the silica and forming a metallic fluoride, as is the case with soda.

Many anhydrous metallic oxides absorb silicon fluoride, becoming hot, and sometimes taking fire.

Potassium and sodium do not react until melted, when they blacken and burn with a dark-red flame, yielding a dark-brown brittle mass (Gay-Lussac and Thénard, Ann. Chim. 69, 204).

Silicon fluoride combines with twice its volume of ammonia gas, forming a volatile crystalline compound $(2\text{NH}_3)\text{SiF}_4$, which is decomposed by water in the following manner:

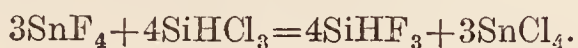


Aniline and a large number of other amines readily react with SiF_4 (Corney and Jackson, Ber. 21, 613; Corney and Smith, *ibid.* 21, 893c). Phosphine combines at -22° and 50 atmospheres pressure to give a white crystalline solid of formula $3\text{SiF}_4 \cdot 2\text{PH}_3$ (Besson, Compt. rend. 110, 80).

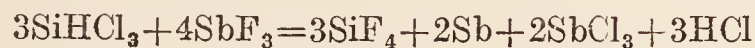
Silicon subfluoride, said to be obtained by passing the tetrafluoride over silicon heated nearly to the softening point of porcelain (Troost and Hautefeuille, Compt. rend. 73, 563) is of doubtful existence.

Hydrofluosilicic acid *v.* FLUORINE. For the refractive index of silicofluorides, see Raiteri (Atti R. Accad. Lincei, 1922, [v.] 31, 1. 112; Chem. Soc. Abstr. 1922, ii. 541).

Silico-fluoroform, *trifluorsilicomethane*, SiHF_3 is prepared by heating silico-chloroform in sealed copper or glass tubes with an equimolecular quantity of tin fluoride or titanium fluoride for 18 hours at $100^\circ\text{--}120^\circ$

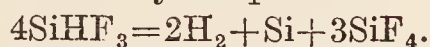


Arsenic and antimony fluorides only yield the tetra-fluoride—

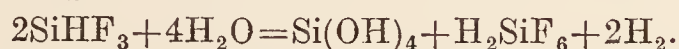


while silver and lead fluorides do not react.

It is a colourless, fuming gas, b.p. -80.2° , m.p. -110° . It slowly decomposes in a sealed tube at the ordinary temperature



It burns with a pale blue flame in air, and decomposes water—



With absolute ethyl alcohol it forms ethyl orthosilicate, and with ether, ethyl silico-orthoformate. It dissolves in its own volume of toluene (Ruff and Albert, Ber. 1905, 38, 53).

SILICON AND CHLORINE.

Silicon tetrachloride SiCl_4 is formed—

1. By heating silicon in chlorine gas (Berzelius, 1824).

2. By passing chlorine over a mixture of finely powdered silica and charcoal made into balls with oil, and strongly heated in a porcelain tube.

3. By the action of chlorine upon magnesium silicide (Gattermann and Weinlig, Ber. 27, 1943), iron silicide (Warren, Chem. News, 66, 113) and other metallic silicides.

Vigouroux (Compt. rend. 1899, 129, 334) prepares it by the action of chlorine at a red heat upon silicon obtained by reducing two parts of silica with one of aluminium, and afterwards treating with (1) hydrochloric acid, (2) aqua regia.

It is a colourless liquid, b.p. 56.9° , m.p. -89° , sp.gr. 1.524. (For other physical properties, v. Thorpe, Chem. Soc. Trans. 1880, 237.)

It is decomposed by water, giving silicic and hydrochloric acids, and by potassium when heated in the vapour, silicon being formed.

If repeatedly passed over silicon heated in a porcelain tube to nearly the softening point of porcelain, with exclusion of air, 'sub-chlorides' were found to be formed by Troost and Hautefeuille (Compt. rend. 73, 563) which could be separated by fractional distillation.

It reacts with ammonia in benzene solution, the product usually isolated being $\text{SiCl}_4 \cdot 6\text{NH}_3$ (v. *Silicon and Nitrogen*).

Molten sulphur trioxide and silicon tetrachloride mix at first without reacting, but the reaction $2\text{SiCl}_4 + 2\text{SO}_3 = \text{Si}_2\text{OCl}_6 + \text{S}_2\text{O}_5\text{Cl}_2$ sets in very slowly in the cold, more rapidly at 50° , and is complete in six to ten hours (Sanger and Riegel, Zeitsch. anorg. Chem. 1913, 80, 252).

Phosphine is not absorbed at ordinary temperatures, but at -23° , 20 volumes are absorbed, which are given off unchanged at 20° . At -80° , 40 vols. (corresponding to $\text{SiCl}_4 \cdot 2\text{PH}_3$), small, highly refractive crystals are formed at 16° under 20 atmospheres pressure, disappearing

at 15 atm. but reforming when the temperature falls to 0° . They are formed at -35° under ordinary pressure. Their composition is not known (Besson, Compt. rend. 110, 240).

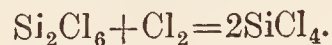
The rate of hydrolysis of silicon chloride is greater than that of the corresponding tin and titanium compounds (v. Kowalewsky, Zeitsch. anorg. Chem. 1900, 25, 189).

Heated with the equivalent quantity of carbon tetrabromide, silicon bromide is formed in 12 p.c. yield (Gustavson, Ann. Chim. [5] 2, 200). With organic compounds a number of organic derivatives have been obtained (q.v.).

Disilicon hexachloride, *hexachlorsilico-ethane*, Si_2Cl_6 is obtained along with the tetrachloride by the action of chlorine upon magnesium silicide, and may be separated by fractional distillation (Gattermann and Weinlig, Ber. 27, 1943). By heating 50 p.c. ferrosilicon in a current of chlorine (Martin, Chem. Soc. Trans. 1914, 2836, 2860). Also by gently heating a mixture of silicon hexaiodide with mercuric chloride, rectifying and purifying by fractional distillation (Friedel, Compt. rend. 73, 1011).

Besson and Fournier (*ibid.* 1909, 148, 839) have obtained it along with other chlorides by submitting silico-chloroform, or silicon tetrachloride mixed with hydrogen to the action of the silent electric discharge.

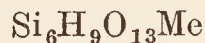
It is a colourless mobile liquid, fuming in moist air; b.p. $145^\circ\text{--}146^\circ$, $144^\circ\text{--}145.5^\circ/760$ mm. (Martin), D_4^{15} 1.5624. Refractive index (D line) 1.4748 at 18° . It crystallises in leaflets at -1° . Its vapour density (Friedel and Ladenburg, Ann. Chim. [5] 19, 390) at 239.4° is 9.7 (air=1). Calculated, 9.29. Dilute ammonia gives hydrogen and silicic acid. Strongly heated it gives off an inflammable vapour, and is completely decomposed on heating to 800° in closed vessels. At 300° it takes fire in chlorine and burns to silicon tetrachloride:



With ammonia in benzene solution, the compound $\text{Si}_2\text{Cl}_6 \cdot 10\text{NH}_3$ is produced, stable up to 100° , but with phosphine reduction takes place even at -10° (Besson, Compt. rend. 110, 516).

With chlorobenzene and sodium, instead of the hexaphenyl derivative, the tetraphenyl derivative is produced, m.p. 231° , which is also the case with silico-chloroform, indicating the great tendency of silicon to form tetra-derivatives (Gattermann and Weinlig, Ber. 27, 1943). With water, *silico-oxalic acid* (q.v.) is produced.

With magnesium methyl iodide disilicon hexachloride forms a yellow compound



(Martin, Ber. 1913, 46, 2442). For the action of disilicon hexachloride upon ethyl alcohol, see Martin, Chem. Soc. Trans. 1914, 2860.

Silicon dichloride Si_2Cl_4 (?) is said to be formed with other products when silicon tetrachloride is passed over heated silicon (Troost and Hautefeuille, Compt. rend. 73, 563). It has not since been investigated.

Trisilicon octachloride, *octachloro-silicopropane*, Si_3Cl_8 has also been separated from the crude silicon tetrachloride obtained by the action of chlorine upon impure silicon prepared

from silica with excess of magnesium by the action of chlorine upon ferrosilicon. Exposed to air, *silico-mesoxalic acid* is produced (Gattermann and Ellery, Ber. 1899, 32, 1114). It is also amongst the products obtained by the action of the silent electric discharge on silico-chloroform. Its m.p. is -67° , and its b.p. 215° – 218° (Besson and Fournier, Compt. rend. 148, 839); 210° – 213° (decomp.), $149^{\circ}/110$ mm. (Martin). $D_4^{15}=1.61$. Refractive index (D line) 1.5135 at 14.5° . For the action of ethyl and methyl alcohols on trisilicon octachloride, see Martin, Chem. Soc. Trans. 1915, 107, 319.

Decachlorosilico-butane $\text{Si}_4\text{Cl}_{10}$, b.p. 149° – $151^{\circ}/15$ mm.

Dodecachlorosilico-pentane $\text{Si}_5\text{Cl}_{12}$, b.p. $190^{\circ}/15$ mm.

Tetradecachloro-silico-hexane $\text{Si}_6\text{Cl}_{14}$, m.p. 170° (decomp. but sublimes *in vacuô* at 200°), and a glassy reddish-yellow residue, stable at 200° and soluble in carbon tetrachloride, probably a mixture of solid chlorides, have also been obtained (Besson and Fournier, *l.c.*; *ibid.* 149, 34).

Silico-chloroform, trichlorosilico-methane, SiHCl_3

is prepared by the action of dry hydrogen chloride upon:—

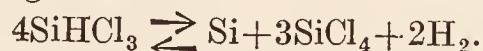
1. Silicon at red heat (Wöhler and Buff, Annalen, 104, 94; Friedel and Ladenburg, *ibid.* 143, 119);

2. Magnesium silicide at 450° – 500° (Gattermann and Weinlig, Ber. 27, 1943);

3. Iron silicide (Warren, Chem. News, 66, 113);

4. Copper silicide (Combes, Compt. rend. 122, 531; Ruff, Albert and Geisel, Ber. 1905, 38, 2222).

The product is condensed by liquid air and freed from silicon tetrachloride by fractional distillation. Where liquid air is not available considerable loss is prevented by absorbing in toluene. It is a colourless liquid, b.p. 33° ; m.p. -134° , sp.gr. 1.3438 at 15° , which fumes strongly in moist air and gives an inflammable vapour. It is completely miscible with CS_2 , CCl_4 , CHCl_3 , SnCl_4 , TiCl_4 , AsCl_3 . It decomposes at 800° , the action being reversible—



It is not attacked at 150° by sodium or other metals.

It reacts with dry oxygen, ozone, sulphuric anhydride, and chromic anhydride, giving oxychlorides. Nitric peroxide at -20° reacts explosively, but in carbon tetrachloride solution the following reaction takes place—

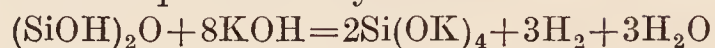


(Besson and Fournier, Compt. rend. 1909, 148, 1192).

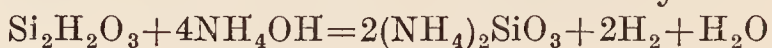
With excess of aniline in benzene solution *trianilino-siliconhydride* $\text{SiH}(\text{NHPh})_3$ is formed (from which SiHCl_3 is regenerated by dry hydrogen chloride) in slender white needles, which begin to decompose at 114° . With ammonia *silicon nitrogen hydride* (*q.v.*) is produced.

With absolute ethyl alcohol it yields *triethyl silico-orthoformate*, b.p. 134° – 137° (Friedel and Ladenburg, Ann. Chim. 1871, [4] 23, 430), and with water *silico-formic anhydride*, a white powder resembling silica, stable at 150° , which

burns in air, and evolves hydrogen on treatment with potassium hydroxide



With ammonia solution it reacts similarly:



It is decomposed by chlorine at ordinary temperatures, giving silicon tetrachloride and hydrogen chloride.

Monochlorosilico-methane SiH_3Cl and *dichlorosilico-methane* SiH_2Cl_2 are obtained by fractionating the difficultly condensable products formed by the action of dry hydrogen chloride upon amorphous silicon. Their b.ps. are about -10° and $+12^{\circ}$ respectively. They are colourless, mobile, highly expansive liquids, which yield hydrogen with water and alkalis.

Silico-hydric chloride, obtained by Wöhler and Buff by passing hydrogen chloride over silicon at low redness, and to which they assigned the formula $\text{Si}_3\text{H}_4\text{Cl}_{10}$ (Annalen, 104, 94), has been shown by Friedel and Ladenburg (Bull. Soc. chim. [2] 7, 322) to be a mixture of silicon tetrachloride and silico-chloroform.

SILICON OXYCHLORIDES.

Considerable interest attaches to these compounds in regard to the constitution of the silicic acids.

Trichlorosilicic oxide $(\text{SiCl}_3)_2\text{O}$ is obtained by passing the vapour of silicon tetrachloride through an exhausted porcelain tube containing fragments of felspar, heated to near the softening point of felspar. On re-passing the vapour several times, and fractionating the product, the oxychloride passes over between 136° and 139° .

It is also formed, together with phosphorus oxychloride, when silicon tetrachloride is passed over strongly heated phosphoric anhydride.

It is a colourless, fuming liquid, of v.d. 10.05 (air=1). It is decomposed by water and alcohol, forming with the latter $[\text{Si}(\text{OC}_2\text{H}_5)_3]_2\text{O}$, b.p. 235° – 237° .

Heated with three molecular proportions of zinc ethyl, *triethylsilicic oxide* $[\text{Si}(\text{C}_2\text{H}_5)_3]_2\text{O}$ is produced (Friedel and Ladenburg, Bull. Soc. chim. [2] 9, 358).

It is also formed from silico-chloroform by the action of dry oxygen or ozone (Besson and Fournier, Compt. rend. 1909, 148, 1192), and when chlorine, mixed with half its volume of oxygen, is passed over heated silicon (Troost and Hautefeuille, Bull. Soc. chim. [2] 35, 360).

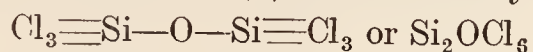
Several oxychlorides are produced by the action of the induction spark on a mixture of the tetrachloride, trichlorosilicic oxide, and oxygen, or by passing trichlorosilicic oxide, together with oxygen, several times over fragments of porcelain heated in a glass tube, the compounds having the molecular formulæ $\text{Si}_4\text{O}_3\text{Cl}_{10}$ and $\text{Si}_4\text{O}_4\text{Cl}_8$, boiling at 153° and 200° respectively, being obtained in largest quantity.

The following have been separated by fractional distillation:—

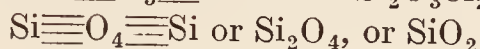
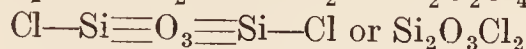
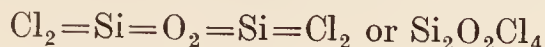
Formula	Boiling-point
1. Si_2OCl_6	136° – 139°
2. $\text{Si}_4\text{OCl}_{14}$	—
3. $\text{Si}_4\text{O}_3\text{Cl}_{10}$	152° – 154°
4. $\text{Si}_4\text{O}_4\text{Cl}_8$	198° – 202°
5. $\text{Si}_4\text{O}_6\text{Cl}_4$	about 400°
6. $\text{Si}_4\text{O}_7\text{Cl}_2$	about 440°
7. $\text{Si}_8\text{O}_{10}\text{Cl}_{12}$	—

(Troost and Hautefeuille, Compt. rend. 73, 563).

The constitution of (1) is undoubtedly

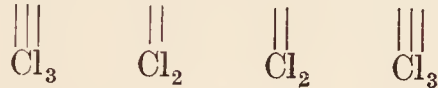
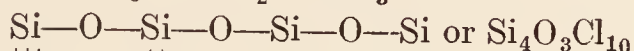
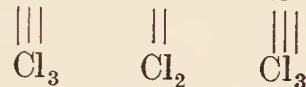
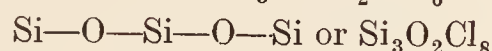
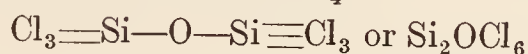


By successive replacement of chlorine by oxygen the following formulæ are derived—



These correspond to the oxychlorides 4 and 5 respectively.

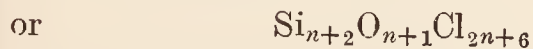
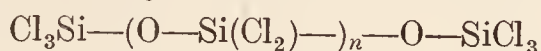
Further, by substitution of the radicle —O—SiCl_3 for chlorine, the following formulæ may be derived from SiCl_4 —



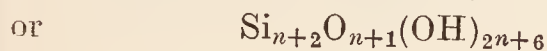
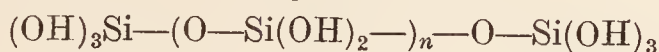
The last corresponds to 3, and by successively replacing pairs of chlorine atoms by oxygen the formulæ $\text{Si}_4\text{O}_4\text{Cl}_8$, $\text{Si}_4\text{O}_5\text{Cl}_6$, $\text{Si}_4\text{O}_6\text{Cl}_4$, and $\text{Si}_4\text{O}_7\text{Cl}_2$, corresponding to 4, 7, 5, and 6 respectively, may be derived.

Formula 2 would appear to be inadmissible.

The above structural formulæ may be written generally—



and the corresponding silicic acids



SILICON AND BROMINE.

Silicon tetrabromide SiBr_4 is produced by passing bromine vapour (1) over an intimate mixture of silica and charcoal (Serullas), (2) over heated silicon, or magnesium silicide (Gattermann, Ber. 22, 186), and (3) in large yield along with silicobromoform, using hydrogen bromide instead of bromine in (2) (Gattermann, *l.c.*).

(4) By heating silicon tetrachloride with carbon tetrabromide (Gustavson, Ann. Chim. [5] 2, 200).

A colourless, fuming liquid, m.p. $+5^\circ$, b.p. $150.8^\circ/751.4$ mm. (Blix), sp.gr. 2.82 (Reynolds) with very regular thermal expansion.

In general properties it resembles the chloride, but differs from it in its vigorous and sometimes explosive reaction with potassium on very slight warming, and in undergoing no reduction when mixed with hydrogen and submitted to the action of the silent electric discharge. It combines with ammonia very slowly, yielding $\text{SiBr}_4 \cdot 7\text{NH}_3$. Phosphine under ordinary pressure does not combine even at solidifying temperature, but on prolonged compression a colourless liquid is formed which changes to a white amorphous solid (Besson, Compt. rend. 110, 240).

Like the chloride, it readily forms organic derivatives.

Monobromo-silico-methane SiH_3Br , b.p. 30° —

40° , and *dibromo-silico-methane* SiH_2Br_2 , b.p. 75° , are spontaneously inflammable liquids obtained in small quantity by fractional distillation of the crude tetrabromide (Besson and Fournier, Compt. rend. 1910, 151, 1055).

Silico - bromoform, *tribromosilico - methane* SiHBr_3 is also obtained thus, but is more easily obtained by the action of dry hydrogen bromide on—

1. Magnesium silicide, although only in small yield, as is the case with silicon and hydrogen bromide, the chief product being the tetrabromide (Gattermann, Ber. 22, 186).

2. Copper silicide (Combes, Compt. rend. 1896, 122, 531).

3. Trianilino-silico-methane (Ruff, Ber. 1908, 41, 3738).

A colourless, fuming liquid, b.p. 109° – 111° , remains liquid at -60° (Besson), sp.gr. 2.7. It is analogous in chemical properties to silico-chloroform, but is less stable than the latter.

Disilicon hexabromide, *hexabromosilico-ethane*, Si_2Br_6 is prepared by adding an equivalent of bromine to a solution of the hexaiodide in carbon disulphide; it crystallises in rhombic plates, which are isomorphous with the corresponding iodide (Friedel and Ladenburg, Ann. Chim. [5] 19, 390). It is also obtained when silico-bromoform is submitted to the action of the silent electric discharge (Besson and Fournier, *l.c.*).

It melts at 95° and boils at 265° .

Octabromosilico-pentane Si_3Br_8 , m.p. 133° , and *decabromosilico-butane* $\text{Si}_4\text{Br}_{10}$, m.p. 185° (decomp.) have also been obtained by this method.

Disilicohydric pentabromide Si_2HBr_5 , m.p. 89° , b.p. 230° (Mahn, Jahresber. 1869, 248), is probably impure Si_2Br_6 .

Trisilicohydric bromide $\text{Si}_3\text{H}_4\text{Br}_{10}$ (Wöhler and Buff, Annalen, 104, 94) is a mixture of SiBr_4 and SiHBr_3 .

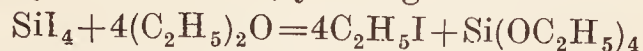
SILICON AND IODINE.

Silicon tetriodide SiI_4 is obtained by passing iodine vapour in a stream of carbon dioxide, through a long porcelain tube filled with silicon and heated to redness. The product sublimes in the cool part of the tube as a white crystalline mass. It is purified by dissolving in carbon disulphide and agitating with mercury.

It crystallises by sublimation or from its solution in carbon disulphide in colourless transparent regular octahedra; mel's at 120.5° to a yellow liquid; boils about 200° , and distils unaltered in a stream of carbon dioxide. Vapour density = 19.12 at 360° . The vapour burns with a red flame, depositing iodine. It is decomposed by water and alcohol.



and by ether at 100° , yielding silicic ether



(Friedel, Annalen, 149, 96).

It has also been prepared by passing iodine vapour with carbon dioxide over the magnesium-silica reduction product at red heat (Gattermann, Ber. 22, 190a).

Disilicon hexaiodide Si_2I_6 . When the tetriodide is heated to 300° with finely divided silver, a white mass is obtained, which is purified by

repeated treatment with small quantities of carbon disulphide and ultimate solution with the aid of heat in that solvent. On cooling, the hexaiodide separates out in colourless hexagonal prisms, which fume on exposure to air. It is decomposed by potash, forming silica, hydriodic acid, and free hydrogen.

It may be fused *in vacuo* at 250°, undergoing partial decomposition (Friedel and Ladenburg, Ann. Chim. [5] 19, 390).

Gently warmed with zinc ethyl it yields on distillation a mixture of silicon tetraethyl, b.p. 150°–154°, and silicon triethyl, b.p. 250°–253°, which may be separated by fractionation (Friedel and Ladenburg, Compt. rend. 68, 920).

Silicon di-iodide Si_2I_4 is described by Friedel and Ladenburg (*ibid.* 68, 920; Bull. Soc. chim. [2] 12, 92), as an orange-red substance, insoluble in CS_2 , CHCl_3 , and SiCl_4 , decomposed by water and evolving hydrogen with potassium hydroxide, produced by the dry distillation of Si_2I_6 .

Silico-iodoform SiHI_3 was prepared by Friedel and Ladenburg (*l.c.*) by passing hydrogen iodide mixed with hydrogen over crystalline silicon and fractionating the product.

It is obtained in fair yield by the action of dry hydrogen iodide on silico-nitrogen hydride suspended in cold carbon disulphide, and, in still better yield, from its action on trianilino-silico-methane in benzene (Ruff, Ber. 1908, 41, 3738).

A colourless, strongly refracting liquid, sp.gr. 3.362 at 0°, 3.314 at 20°. It boils at 220°, but decomposes slowly above 150°, and if kept boiling the temperature gradually rises to 300°, the residue being the tetraiodide. It can, however, be distilled under reduced pressure. It is decomposed by water in a manner similar to silico-chloroform.

Hydrosilicic iodide is the name given by Wöhler and Buff to the substance obtained by passing hydriodic acid over heated crystalline silicon (Annalen, 104, 99). This has been shown by Friedel and Ladenburg (*l.c.*) to be a mixture of silicic iodide, free iodine, and silico-iodoform SiHI_3 .

MIXED HALOGEN DERIVATIVES.

Silicon chlorobromides. A **trichlorobromide** SiCl_3Br is obtained by the action of bromine upon silicic chloroform. It is a colourless, fuming liquid, boiling at 80°, and decomposed by water. A **dichlorobromide** SiCl_2Br_2 is also formed in the above reaction, and is found amongst the products boiling at 100° (Friedel and Ladenburg, Ann. Chim. [4] 27, 416).

The **trichlorobromide** is also obtained without the second product by the action of Br upon the trichlorosulphydrate (*q.v.*) (Friedel and Ladenburg, *l.c.*).

SiClBr_3 was obtained by Reynolds from the tetrabromide (Chem. Soc. Trans. 1887, 590).

They may also be obtained by passing a mixture of hydrogen bromide and silicon chloride through a red-hot tube, shaking the condensed product with mercury and fractionating (Besson, Compt. rend. 112, 788; 1911, 152, 603).

Silicon chloroiodides. The three chloroiodides are present in the product obtained by

passing iodine chloride vapour over crystalline silicon at nearly red heat (Besson, *ibid.* 112, 1314). They are also formed when hydrogen iodide and silicon chloride vapour are passed through glass tubes heated to redness (Besson and Fouriner, Compt. rend. 1911, 152, 603).

The **trichloroiodide** is also formed by heating silicon chloride and iodine in sealed tubes at 200°–250°, and the **dichloroiodide** by saturating the trichloroiodide with hydrogen chloride at –22°, and heating in sealed tubes at 250°.

They are colourless, fuming liquids, liberating iodine on exposure to light, and burn with liberation of iodine (Besson, *ibid.* 611). Silicon bromoiodides are obtained by distilling iodine bromide over crystalline silicon at nearly red heat, and fractionating the product over copper.

The **tribromoiodide** results on heating silico-bromoform with iodine in sealed tubes at 200°–250°, and from the action of hydrogen iodide on silicon bromide at red heat (Besson, *ibid.* 1447).

The mixed halogen compounds, like the simple ones, give definite compounds with ammonia.

The melting- and boiling-points of the above compounds, as determined by Besson, are tabulated below—

Formula	M.p.	B.p.
SiCl_3Br	—	80°
SiCl_2Br_2	—	103°–105°
SiClBr_3	–39°	126°–128°
SiCl_3I	—	113°–114°
SiCl_2I_2	—	172°
SiClI_3	2°	234°–237°
SiBr_3I	14°	192°
SiBr_2I_2	38°	230°–231°
SiBrI_3	53°	255°

SILICON AND NITROGEN.

Silicon nitrides. Deville and Wöhler obtained by the action of ammonia on silicon chloride, and by strongly heating crystalline silicon in nitrogen on air, a white amorphous infusible mass, indifferent to most reagents, although slowly evolving ammonia in moist air, which they concluded to be silicon nitride without, however, ascertaining its composition (Annalen, 104, 256; 110, 248).

By heating crystalline silicon with gas carbon in a blast furnace Schützenberger (Compt. rend. 89, 644) obtained a mixture of silica with a green and a white substance, to which he assigned the formulæ $(\text{SiN})_x$ and Si_3N_4 respectively, the former being insoluble in hydrofluoric acid, the latter soluble.

By heating crystalline silicon in pure nitrogen, and treating the white mass so produced with potassium hydroxide, and then with hydrofluoric acid, a residue is obtained having the composition Si_2N_3 (Schützenberger and Colson, Compt. rend. 93, 1508).

According to Weiss and Engelhardt (Zeitsch. anorg. Chem. 1909, 65, 38) silicon begins to combine with nitrogen at about 1240°, the rate of combination increasing rapidly with rise of temperature. The bulky amorphous product consists of nitrides mixed with silicon.

Silicon mononitride SiN is the residue remaining when the product is boiled with a

mixture of nitric and hydrofluoric acids and then ignited and washed with hydrochloric acid. It is white and of sp.gr. 3.17.

Silicon sesquinitride Si_2N_3 is obtained if the crude product is boiled first with potassium hydroxide, and then with hydrofluoric acid. It still contains silica which cannot be removed. Its sp.gr. is 3.64.

Trisilico-tetranitride Si_3N_4 , sp.gr. 3.44, is formed when silicon is heated in nitrogen at 1300° – 1400° , until saturated, and is only slightly decomposed by treatment with potassium hydroxide, hydrofluoric acid, or a mixture of hydrofluoric and nitric acids. The other nitrides are readily attacked. The sesquinitride is converted by the latter mixture into the mononitride (*v. also Siliconimide*).

By heating silicon in the flame of a coke fire a substance having approximately the formula $\text{Si}_3\text{C}_3\text{N}$ is formed (*l.c.*).

Siliconamide $\text{Si}(\text{NH}_2)_4$ is the first product obtained in the reaction between benzene solutions of silicon chloride and ammonia (Lengfield, Amer. Chem. J. 1899, 21, 531; *v. also* Ruff, Ber. 1908, 41, 3744). It is a white solid, easily losing ammonia and yielding

Siliconimide $(\text{SiNH})_2$. The product usually isolated is $\text{SiCl}_4 \cdot 6\text{NH}_3$, which, as it loses one-third of its ammonia when thrown into water, may be looked upon as $\text{Si}(\text{NH})_2 \cdot 4\text{HN}_4\text{Cl}$ (Lengfield, *l.c.*; *v. also* Gattermann, Ber. 22, 186). It is probably identical with

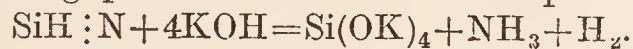
Silico-cyanamide $\text{SiN} \cdot \text{NH}_2$, described by Harris (Chem. Zentr. 1899, ii. 283) as obtained by the action of dry ammonia upon silicon chloride.

According to Blix (Ber. 1903, 36, 4220) $\text{Si}(\text{NH})_2$ is also obtained by the action of liquid ammonia on silicon thiochloride. When heated to 900° it loses ammonia and leaves Si_2HN_3 .

For the silicon analogue of calcium cyanamide, *see* Wohler and Bock (Zeitsch. anorg. Chem. 1924, 134, 221; Chem. Soc. Abstr. 1924, ii. 473).

Silicon nitrimide $\text{Si}_2\text{N}_3\text{H}$ (*cf.* Schützenberger and Colson, Compt. rend. 92, 1508), which further loses ammonia at 1200° – 1300° , leaving Si_3N_4 .

Silico-nitrogen hydride $\text{SiH} : \text{N}$ is the product obtained by washing with liquid ammonia the powder obtained by the action of dry ammonia diluted with hydrogen, on silico-chloroform at -10° . With water or potassium hydroxide the following quantitative reaction takes place—



It possesses the reducing properties of silicoformic anhydride, and is converted by dry hydrogen chloride at 300° into silico-chloroform and ammonium chloride (Ruff, Albert and Geisel, Ber. 1905, 38, 53).

The substance $\text{Si}_5\text{N}_6\text{Cl}_2$ is formed as a white powder when the product of the reaction of dry ammonia upon silicon chloride is heated to redness in a current of hydrogen. On heating this to redness in a current of ammonia it loses chlorine, and is converted into $\text{Si}_2\text{N}_3\text{H}$ (Schützenberger and Colson, Compt. rend. 92, 1508).

SILICON AND CARBON.

Silicon carbide *v.* CARBORUNDUM. For details of manufacture, &c., *see* Brockbank, J. Soc. Chem. Ind. 1920, 39, 41 T.

Silicon dicarbide SiC_2 is formed by passing ethylene, or hydrogen saturated with benzene, over silicon heated to whiteness in a porcelain tube. It is attacked not by acids, nor by oxygen or chlorine at red heat, but is decomposed by fused potassium hydroxide, or a mixture of lead oxide and chromate (Colson, Compt. rend. 94, 1316, 1526).

Oxycarbides of the formulæ SiCO , SiCO_2 , SiCO_3 , $\text{Si}_2\text{C}_2\text{O}$, $\text{Si}_2\text{C}_3\text{O}$, $\text{Si}_2\text{C}_3\text{O}_2$, and $\text{Si}_2\text{C}_4\text{O}_4$ have been prepared (Colson and Schützenberger, *ibid.* 93, 1508; Colson, *ibid.* 94, 1316, 1526).

Siloxicon. The commercial name for the product obtained by Acheson in 1899 by electrically heating together graphite and silica. Is a mixture of silicon carbide and oxycarbides. It is highly refractory, and eminently suitable for resistant crucibles, firebricks, furnace linings, &c., but is not now used to any extent (J. Soc. Chem. Ind. 1910, 245).

A sample gave on analysis—

$\text{Si}_2\text{C}_2\text{O}$, 71.39 p.c.; SiCO_3 , 10.81 p.c.; SiC , 5.81 p.c.; graphite, 10.66 p.c.; Fe, 1.07 p.c.; impurities, 0.86 p.c. (Spielmann, *ibid.* 1905, 24, 654).

The substances $\text{Si}_4\text{C}_4\text{S}$ and $\text{Si}_2\text{C}_2\text{N}$ have also been described (Colson, Compt. rend. 94, 1316, 1526; Schützenberger and Colson, *ibid.* 92, 1508).

Silicon thiocyanate was obtained by Miguel (Ann. Chim. 1877, [v.] ii. 343) by heating lead thiocyanate with silicon tetrachloride to about 350° . Reynolds (Chem. Soc. Trans. 1906, 397) obtains a better yield by heating 100 grms. of the dehydrated and powdered salt with 17 grms. of silicon chloride in 400 c.c. of benzene on the water-bath with reflux condenser. The hot liquid is filtered and after distilling off a portion of the benzene, crystallised, m.p. 143.8° , b.p. 314.2° . Stable at red heat, v.d. 259° ($\text{Si}(\text{SCN})_4$ 260°). Its stability shows it to be $\text{Si}(\text{SCN})_4$ rather than $\text{Si}(\text{NCS})_4$.

SILICON AND PHOSPHORUS.

Silicon phosphide is formed according to Gewecke (Annalen, 1908, 361, 89) by the action of phosphine upon silicon chloride. *See, however,* Besson under *Silicon chloride*.

Silicon phosphate. When precipitated silica is dissolved in fused metaphosphoric acid, and the mass extracted with water, transparent, colourless octahedra are obtained, sp.gr. 3.1, which scratch glass, and melt on platinum under the blow-pipe to a glass which does not devitrify on cooling; formula $\text{SiO}_2 \cdot \text{P}_2\text{O}_5$. It exists also as hexagonal crystals and monoclinic prisms, and also in the hydrated form $\text{SiO}_2 \cdot \text{P}_2\text{O}_5 \cdot 4\text{H}_2\text{O}$ (Hautefeuille and Margottet, Compt. rend. 96, 1052; 99, 780; 104, 56).

SILICON AND BORON.

Silicon triboride and **silicon hexaboride** are produced by heating 1 part of boron with 5 parts of silicon electrically in a clay crucible for about a minute. The residue after treating with a mixture of nitric and hydrofluoric acids, then with hot potassium hydroxide, and finally with dilute nitric acid, yields the two borides SiB_3 and SiB_6 with 80–90 p.c. of the latter.

The hexaboride is readily oxidised by boiling nitric acid, while the triboride is very slowly

attacked, but the latter is decomposed by fused potassium hydroxide, which leaves the former unchanged. Thus both can be obtained in pure condition.

SiB_3 forms black rhombic plates, sp.gr. 2.52.

SiB_6 forms black opaque irregular crystals, sp.gr. 2.47.

Both are decomposed by fluorine on warming, and by chlorine and bromine at a higher temperature, but not by iodine or nitrogen or by halogen acids. They are superficially oxidised in air, and readily decomposed by potassium carbonate or fusion mixture (Moissan and Stock, Compt. rend. 1900, 131, 139).

SILICON AND SULPHUR.

Silicon disulphide SiS_2 was first prepared by Berzelius, by the union of sulphur and amorphous silicon.

It is produced by passing the vapour of carbon disulphide over a mixture of silica and lampblack made into balls and ignited, and is deposited in the cool parts of the tube in asbestiform needles (Fremy, Ann. Chim. [3] 38, 314).

When dry hydrogen sulphide is passed over crystallised silicon at a red heat, fine white needles of the disulphide are produced. A yellowish sublimate is formed at the same time, probably consisting of Si_3S_4 (Sabatier, Bull. Soc. chim. [2] 38, 153).

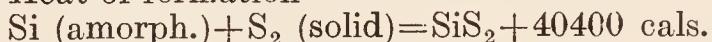
It is formed in the decomposition of silicon thiochloride (Blix, Ber. 1903, 36, 4218).

Fielding (Trans. Faraday Soc. 1909, 5, 110) obtained it in an impure state by heating ferrosilicon with ferrous sulphide in a vacuum.

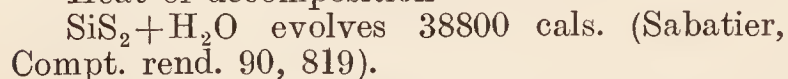
It is best prepared by heating amorphous silicon with three times the quantity of sulphur at 150° , and afterwards at a red heat. It is purified by subliming in a porcelain tube under reduced pressure (60 mm.) (Hempel and Haasy, Zeitsch. anorg. Chem. 23, 32).

When pure it forms white needle-shaped crystals, which sublime unchanged. It decomposes rapidly in contact with moist air, forming hydrogen sulphide and silica. Alcohol and ether act upon it in the cold. Nitric acid decomposes it, with separation of sulphur, and formation of silicic and sulphuric acids. Hydrogen has no action upon it (Fremy). It combines readily with sodium sulphide (Hempel and Haasy), and with potassium sulphide (Berzelius).

Heat of formation—



Heat of decomposition—

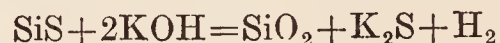


Silicon monosulphide SiS is obtained as a yellow sublimate, together with another yellowish substance, an oxysulphide SiSO , on passing carbon disulphide vapour over silicon at a white heat.

If the contents of the tube are treated with potash and hydrofluoric acid, a greenish powder is obtained having the composition $\text{Si}_4\text{C}_4\text{S}$, which is converted into $\text{Si}_4\text{C}_4\text{O}_2$ by heating in a current of oxygen (A. Colson, Bull. Soc. chim. [2] 38, 56; Compt. rend. 94, 1526).

In addition to SiSO another oxysulphide SiSO_2 has been investigated (Rankin and Revington, Chem. Soc. Proc. 1908, 131).

Cambi (Atti R. Accad. Lincei, 1910, [v.] 19, ii. 294; *ibid.* 1911, [v.] 20, i. 433), by heating ferrosilicon and sulphur in an electric furnace, and subliming the grey mass so formed, obtained the monosulphide in two forms, as a black vitreous solid, and as a yellow powder. Either form gives both on sublimation. The black variety is of sp.gr. 1.853. Both forms are decomposed by alkalis as follows:



and with water they evolve hydrogen sulphide and leave residues of uncertain composition.

A **silico-hydric sulphide** $\text{Si}_4\text{H}_8\text{S}_5$, corresponding to the oxygen compound, is formed by the action of aqueous sulphurous acid mixed with a little hydrochloric acid upon calcium silicide (Wöhler, Annalen, 127, 257).

A **sulphochloride** of silicon was obtained by Pierre, who gave it the formula $\text{Si}_3\text{S}_4\text{Cl}_8$, by passing a mixture of silicon chloride vapour and dry sulphuretted hydrogen gas through a red-hot porcelain tube, distilling the product, and collecting what passed over at 90° – 100° (Pierre, Annalen, 69, 73).

Friedel and Ladenburg assign to it the name *silicon chlorosulphydrate* and the formula SiCl_3SH or *silico-trichloromercaptan*. It is a colourless liquid, boiling at 96° , decomposing on exposure to the air into hydrochloric and sulphydric acids and silica. With alcohol, in the proportion of 3 mols. alcohol and 1 mol. of the body, it forms $\text{SiSH}(\text{OC}_2\text{H}_5)_3$, but an excess of alcohol converts it into silicic ether $\text{Si}(\text{C}_2\text{H}_5\text{O})_4$.

With bromine it forms a trichlorobromide (Friedel and Ladenburg, Ann. Chim. [4] 27, 416; *v.* also Bull. Soc. chim. [2] 7, 472).

At higher temperatures the action of silicon chloride on hydrogen sulphide gives **silicon thiochloride** SiSCl_2 , which, crystallised from chloroform, melts at 75° and boils at $92^\circ/22.5 \text{ mm.}$ It decomposes on boiling into SiS_2 and SiCl_4 , and with liquid ammonia gives $\text{Si}(\text{NH})_2$ (Blix, Ber. 1903, 36, 4218).

It is also formed along with SiS_2 by passing chlorine and sulphur chloride vapour over crystalline silicon at bright-red heat. It can be sublimed in a current of dry air at 100° (Besson, Compt. rend. 113, 1040).

Silicon thiobromide SiSBr_2 is obtained from silicon bromide and hydrogen sulphide at 150° in presence of aluminium bromide, m.p. 93° , b.p. $150^\circ/18.3 \text{ mm.}$ Dry ammonia in benzene solution yields *silicon thiourea* $\text{SiS}(\text{NH}_2)_2$ (Blix, *l.c.*).

Silicon selenide SiSe_2 is produced by passing dry hydrogen selenide over crystalline silicon at a red heat, as a semi-metallic lustrous hard mass with an irritating odour. It is decomposed by cold water, more readily by potash, evolving hydrogen selenide. It is converted by oxygen at a red heat into silica, selenious anhydride and selenium (Sabatier, Compt. rend. 113, 132).

Wöhler (Annalen, 127, 257) describes compounds of selenium and tellurium analogous to the silico-hydric sulphide described above.

METALIC SILICIDES.

Magnesium, calcium, strontium, and barium reduce the oxide with formation of silicides. Crystalline silicides have been prepared from

iron, chromium, nickel, cobalt, manganese, copper, platinum, and other metals, usually by direct union of the elements, or by heating the metal in silicon chloride vapour.

Potassium, sodium, aluminium, zinc, lead, tin, bismuth, antimony, gold, and silver dissolve silicon when in the molten state, but re-deposit it on cooling, without forming compounds.

Lithium silicide Li_6Si_2 is remarkable in that with concentrated hydrochloric acid *silico-hexane* Si_2H_6 is evolved. Dilute acid gives hydrogen. Heated in dry hydrogen chloride, lithium and silicon chlorides are formed and hydrogen liberated (Moissan, Compt. rend. 1902, 135, 1284).

Calcium silicide CaSi_2 was obtained by Wöhler by heating together graphitoidal silicon (300 grms.), calcium chloride (3000 grms.), and sodium (350 grms.) covered with another 350 grms. of sodium, and, lastly, with a layer of common salt, in a covered crucible, to bright-red heat (Annalen, 126, 257). It is thus obtained as a button with metallic lustre, lead grey colour, and scaly crystalline structure, crumbling on exposure to air.

It is also formed by heating silicon and lime in an ordinary furnace with calcium fluoride or chloride as flux (Goldschmidt, D. R. P. 199193), or with carbon in the electric furnace (de Chalmot, Amer. Chem. J. 1896, 18, 536). With water and dilute acids hydrogen is evolved, but little, if any, silicon hydride (*v. however*, Bradley, Chem. News, 82, 149; Chem. Zentr. 1900, ii. 890).

According to Le Chatelier (Bull. Soc. chim. 1897, [iii.] 17, 793), it exists in two varieties, the first scarcely attacked by concentrated nitric acid, and leaving a yellow *silicone* on treatment with hydrochloric acid; the second readily attacked by nitric acid, and giving a white residue with hydrochloric acid. Usually a mixture of these residues is obtained, the composition of which varies from $\text{Si}_2\text{O}_4\text{H}_4$ to $\text{Si}_2\text{O}_3\text{H}_4$.

Tricalcium disilicide Ca_3Si_2 is described by Hackspill (*ibid.* 1908, [iv.] 3, 619) as being obtained by compressing a mixture of calcium filings and powdered silicon into a calcium cylinder enclosed in one of iron, and heated to 1000° in a porcelain tube. Excess of calcium is removed by sugar solution, and the slender needles of the silicide washed with alcohol and ether, sp.gr. 1.64. This silicide is attacked by halogens in the cold, and by oxygen at red heat. Dilute acids give spontaneously inflammable hydride, as with lithium silicide (*v. also* Hönigschmid, Monatsh. 1909, 30, 497).

Several alloys have been prepared by Tamaru (Zeitsch. anorg. Chem. 1909, 62, 81).

Strontium silicide SrSi_2 is prepared like the corresponding calcium compound, but according to Bradley (*l.c.*) differs from the latter in that no silico-acetylene is evolved with acids.

Barium silicide BaSi_2 . Barium peroxide and silicon react violently when the action is initiated by means of a fuse. With 50 parts BaO_2 and 15 parts Si, a barium silicide containing 30 p.c. Ba is obtained (Askenasy and Ponnaz, Zeitsch. Elektrochem. 1908, 14, 810).

Barium chloride (and also other difficultly volatile chlorides, as those of calcium and manganese) give the silicide when heated with

silicon in the electric furnace (Jüngst and Mewes, D. R. P. 15716). They yield hydrogen silicide with dilute or concentrated hydrochloric acid.

Magnesium silicide. According to Wöhler (*l.c.*), when magnesium chloride, sodium chloride, sodium silicofluoride, and metallic sodium are fused together for the preparation of silicon hydride, the mass contains, besides free silicon, two magnesium silicides, one of which yields silicon hydride with aqueous ammonium chloride or hydrochloric acid, whilst the other yields hydrogen and silica.

Lebeau and Bossnet (Rev. Metallurgie, 1909, 6, 272), however, as a result of microscopic examination of the various products obtained by heating magnesium, alone and with silicon under potassium silicofluoride, state that only one silicide Mg_2Si exists (*v. further* Winckler, Ber. 23, 2642). It is of slate-blue colour, sp.gr. 2, decomposes cold water slowly with liberation of hydrogen, and with dilute hydrochloric acid yields a mixture of hydrogen and silicon hydrides.

It is also prepared (Moissan and Smiles, Ann. Chim. 1902, 7, 5) by heating to redness a mixture of silicon and magnesium powder in a porcelain tube in a current of hydrogen, but is most conveniently obtained in a crude form by heating a mixture of sand and magnesium powder in the requisite proportions (*v. Silicon, Preparation of*), m.p. 1102° (Vögel, Zeitsch. anorg. Chem. 1909, 61, 46). Eutectics are formed with 48 p.c. and 4 p.c. of silicon respectively.

Copper silicide. Three products with different silicon content were obtained by Deville and Caron (Annalen, 104, 232; Ann. Chim. [iii.] 67, 455), but were not definite compounds. Cu_2Si_3 (de Chalmot, Amer. Chem. J. 1896, 18, 95; 1897, 19, 118) and Cu_2Si (Vigouroux, Compt. rend. 1896, 122, 318) have also been described, but according to Lebeau (*ibid.* 142, 154) only

Cuprous silicide Cu_4Si exists, any excess of silicon being uncombined, and in a form insoluble in hydrofluoric acid (*cf.* Moissan and Siemens, *ibid.* 1904, 138, 1299).

The freezing-point curve for Cu and Si shows only one maximum (at 800°) corresponding to Cu_4Si .

It is obtained by fusing together silicon (17 parts) and electrolytic copper (90 parts) in a current of hydrogen, and extracting the uncombined silicon with 5 p.c. sodium carbonate (*v. also* Vigouroux, *ibid.* 1907, 144, 1214; Phillips, Metallurgie, 1907, 4, 587, 613). It is silver-white, turning brick-red on exposure, sp.gr. 7.48 (Vigouroux, Compt. rend. 1906, 142, 87; *cf.* Sanfourche, Rev. Met. 1919, 16, 246).

Cementation of copper turnings can be effected at 700° with absorption of 9.56 p.c. of silicon.

A dark copper-coloured silicide is said to be formed when copper sulphate is precipitated with silicon hydride. It is readily oxidised, and is decomposed at once by nitric acid.

Silicides of silver have been described, but according to Arrivaut (Compt. rend. 1908, 147, 859) are non-existent.

Aluminium and silicon do not combine, though miscible in all proportions in the fused state. The eutectic (10 p.c. Si) melts at 576°

(Minet, *ibid.* 112, 1215; Kieser, Chem. Zeit. 1908, 32, 1161; Fraenkel, Zeitsch. anorg. Chem. 1908, 58, 154; Roberts, Chem. Soc. Trans. 1914, 105, 1383).

It, however, forms double silicides with a number of other metals (Lévy, Compt. rend. 106, 66; Vigouroux, *ibid.* 141, 951; Manchot and Kieser, Annalen, 1904, 337, 353; Manchot and Fischer, *ibid.* 1907, 357, 129).

Tin, lead, and thallium form no compounds with silicon (Tamaru, Zeitsch. anorg. Chem. 1909, 61, 40).

Titanium silicide TiSi_2 is produced from the oxide or potassio-fluoride with sand, aluminium, and sulphur, ignited by a Goldschmidt cartridge (U.S. Pat. 923, 152).

Zirconium silicide ZrSi_2 is prepared similarly (Hönigschmid, Compt. rend. 1906, 143, 224).

Cerium silicide CeSi_2 is obtained together with potassium at the negative pole on electrolysis a fused mixture of potassium fluoride and cerium oxide, and after removal of the potassium with alcohol, remains as a brown powder, insoluble in acids, which burns with a reddish flame (Ulik, Chem. Zentr. 1865, 1045). Prepared by fusing the oxide with silicon in the electric furnace, it differs from the above in being definitely crystalline, and attacked by mineral acids with disengagement of hydrogen (Sterba, Compt. rend. 1902, 135, 170).

Solid silicon floats on molten cerium, and at a sufficiently high temperature (*circa* 1400°) combines explosively forming CeSi , melting above 1500° . This compound forms yellow, rounded crystallites, and the eutectic has a distinct lamellar structure. The alloys are brittle, very stable in air, and are not pyrophoric (Vogel, Zeitsch. anorg. Chem. 1913, 84, 323).

Thorium silicide ThSi_2 is obtained by heating the double fluoride of potassium and thorium, potassium silicofluoride, and aluminium, at 1200° (Hönigschmid, *ibid.* 1906, 142, 157).

It closely resembles graphite; sp.gr. 7.96.

Vanadium silicides. Two silicides are known, VSi_2 (Moissan and Holt, *ibid.* 1902, 135, 78) and V_2Si (*ibid.* 493), produced by heating together vanadium sesquioxide and silicon in the electric furnace. If silicon is in excess the former is obtained, and the latter, produced when excess of V_2O_3 is used, is converted into the former by heating with excess of silicon. VSi_2 is a brilliant metallic crystalline substance, sp.gr. 4.42, harder than glass, melts at 1655° , and is volatile in the electric furnace. V_2Si , obtained in metallic silvery prismatic crystals, sp.gr. 5.48, is harder and less volatile than VSi_2 . Both are somewhat refractory towards most reagents, but are readily attacked by hydrofluoric acid (*v.* further Moissan and Holt, Ann. Chim. 1902, vii. 27, 277; Gin, Electrochem. and Met. Ind. 1909, 7, 264; Giebelhausen, Zeitsch. anorg. Chem. 1915, 91, 251).

Tantalum silicide TaSi_2 , *v.* Hönigschmid (Monatsh. 1907, 28, 1017).

Chromium silicides. Cr_2Si is obtained by heating the metal or its oxide with silicon in the electric furnace (Moissan, Compt. rend. 1895, 121, 621).

Cr_3Si_2 is obtained by prolonged heating of silicon chloride with pure chromium at 1200° (Vigouroux, *ibid.* 1907, 144, 83).

Cr_3Si (Zettl, *ibid.* 1898, 126, 833), Cr_2Si , and

CrSi_2 (de Chalmot, Amer. Chem. J. 1897, 19, 69) are all obtained by fusing copper and the requisite proportions of chromium and silicon together (Lebeau and Figueras, Compt. rend. 1903, 136, 1329).

Molybdenum silicide MoSi_2 , sp.gr. 6.2 (Defacqz, *ibid.* 1907, 144, 1424).

Tungsten silicide WSi_2 , sp.gr. 9.4 (*ibid.* 848), and **Uranium silicide** USi_2 , sp.gr. 8 (*ibid.* 1908, 147, 1050), have been prepared by direct union of the elements, or by reaction of the oxide with silicon in the electric furnace.

Manganese silicides. Indefinite products, containing 0.6–13 p.c. of silicon, were obtained by Wöhler (Annalen, 106, 54).

Mn_2Si is obtained by heating together (1) quartz, manganese dioxide, and carbon, (2) silicon and manganese dioxide, (3) silicon and manganese, in the electric furnace (Vigouroux, Compt. rend. 1895, 121, 771); and also by fusing an alloy of copper and silicon with manganese in the electric furnace (Lebeau, *ibid.* 1903, 136, 89). The product is purified by extracting with nitric acid, and then 10 p.c. soda, yielding lustrous prisms, sp.gr. 6.4, decomposed by dilute hydrochloric acid. MnSi , found by Carnot and Goutal in the residue left after the action of sulphuric acid on ordinary castings (Ann. des Mines, 1900, [ix.] 18, 271), is obtained as above, using a larger proportion of silicon. Lustrous, tetrahedral crystals, sp.gr. 5.9, only slowly attacked by hydrochloric acid (Lebeau, *l.c.*; Ann. Chim. 1904, [viii.] 1, 553). MnSi_2 is obtained by still further increasing the proportion of silicon, as octahedral crystals, sp.gr. 5.24 (Lebeau, *ibid.* 1903, 136, 231).

The freezing-point curve for Mn, Si, shows two maxima, corresponding to Mn_2Si and MnSi respectively (Doerincel, Zeitsch. anorg. Chem. 1906, 50, 117).

Iron silicides. Silicon is almost always present in cast iron, owing to reduction of silica in smelting. In white cast iron the amount is usually 0.1 to 0.5 p.c., and in grey 0.5 to 3 p.c.

Fe_2Si , first described by Hahn (Annalen, 129, 57), is obtained by heating iron with one-tenth its weight of silicon, or ferric oxide with excess of silicon, in the electric furnace. After extracting with nitric acid (1:4) small magnetic prismatic needles remain, sp.gr. 7 (Moissan, Compt. rend. 1895, 121, 621). It is also produced by Lebeau's method, *v.* Mn_2Si , and Compt. rend. 131, 583, and by the action of silicon chloride on iron at white heat (Vigouroux, *ibid.* 1905, 141, 828).

FeSi was obtained by Vanzetti (Gazz. chim. ital. 1906, 36, i. 498) as a button on heating a mixture of coke, sand, and lime to 3000° .

The existence of Fe_2Si and FeSi is confirmed by the freezing-point curve (Guertler and Tammann, Zeitsch. anorg. Chem. 1905, 46, 163), and by the magnetic attraction curve (Jouve, Compt. rend. 1902, 134, 1577).

FeSi_2 (de Chalmot, Amer. Chem. Soc. 19, 118; Lebeau, Compt. rend. 1901, 133, 1008) and FeSi_3 (Naske, Chem. Zeit. 1903, 27, 481) are also said to exist, but only in presence of excess of silicon. Fe_3Si_2 and Fe_5Si_2 are not definite compounds (Carnot and Goutal, Compt. rend. 125, 148; Jouve, Bull. Soc. chim. [3] 25, 290). Cementation with silicon takes place at 950° (Lebeau, Bull. Soc. chim. 1902, 27, 44).

Commercial ferrosilicon has been found to evolve poisonous and explosive gases. The alloy containing about 50 p.c. Si is sensitive to water and very dangerous (cf. Kurnakow and Urasow, *Zeitsch. anorg. Chem.* 1922, 123, 89).

Crystalline silicon displaces carbon almost completely from cast iron as graphite (Moissan, *Compt. rend.* 1894, 119, 1172; Sanfourche, *Rev. Mét.* 1919, 16, 239).

For the structural constitution of iron-carbon silicon alloys, see Honda, Murakami (*Sci. Rep. Tôhoku, Imp. Univ.* 1924, 12, 257; *Chem. Soc. Abstr.* 1924, 126, ii. 556).

For the effect of silicon on the dilatation of steels, see Charpy and Cornu, *Compt. rend.* 1913, 156, 1240; 157, 319; Vigouroux, *ibid.* 1913, 156, 1374; Charpy and Cornu-Thenard, *J. Iron and Steel Inst.* 1915, 91, 276; Andrew, *ibid.* 1916, 7, 1. *Silicol* is a mixed silicide of iron and aluminium used for the generation of hydrogen (see HYDROGEN). A commercial specimen examined by Joubert (*Rev. gen. Chim. pure. Appl.* 1913, 16, 341) had the composition Si, 70.35; Fe, 11.90; Ti, 3.55; Al, 14.05.

Nickel silicides. Ni_4Si is obtained by the action of silicon chloride upon nickel, and on prolonged action of the chloride is changed to Ni_2Si (Vigouroux, *Compt. rend.* 1906, 142, 1270). Guertler and Tammann (*Zeitsch. anorg. Chem.* 1906, 49, 93) from the Ni-Si freezing-point curve, infer the existence of Ni_3Si , Ni_2Si , Ni_3Si_2 , NiSi , and Ni_2Si_3 .

Cobalt silicides. Silicon chloride passed over metallic cobalt at 1200° – 1300° yields Co_2Si (Vigouroux, *Compt. rend.* 1906, 142, 635). CoSi , CoSi_2 , CoSi_3 , and Co_3Si_2 are also said to exist (Lewkonja, *Zeitsch. anorg. Chem.* 1908, 59, 293).

Palladium silicides. PdSi , obtained in small brilliant bluish-grey fragments of sp.gr. 7.3, is the only silicide isolated, but the Pd-Si freezing-point curve gives two maxima, at 1400° and 990° , corresponding to SiPd_2 and SiPd respectively (Lebeau and Jolibois, *Compt. rend.* 1908, 146, 1028).

Platinum silicides. PtSi is formed by direct union of platinum and silicon. Crystallised from molten silver-silicon alloy, the latter being subsequently removed by successive treatment with sodium hydroxide and nitric acid, it is obtained in fine prismatic crystals, sp.gr. 11.63, m.p. about 1100° . After heating with tin, and extracting with potassium hydroxide, a residue of Pt_2Si is left (Lebeau and Novitzky, *Compt. rend.* 1907, 145, 241; v. also Vigouroux, *ibid.* 1907, 145, 376). PtCu_2Si results on heating platinum and copper silicides together.

According to Warren and Vigouroux, gold forms an alloy with silicon. Di Capua, however, states that whilst gold and silicon are miscible in all proportions in the liquid condition they form no compounds. The melting-point of gold is lowered by about 800° by 6–7 p.c. of silicon (Di Capua, *Atti R. Accad. Lincei*, 1920, [v.] 29, i. 111).

A number of the silicides above mentioned may be prepared by heating the oxide of the metal with silicon carbide (Baraduc-Muller, *Rev. Mét.* 1910, 7, 657).

The constitution of certain silicides is dis-

cussed by Manchot (*Annalen*, 1905, 342, 356; 1907, 357, 129).

SILICON BRONZE v. TIN.

SILK. Silk consists of a continuous thread produced by a caterpillar, the silkworm, to form the cocoon in which it envelops itself before entering the pupal state. There are several kinds of silkworms, all of which are included in the natural order *Lepidoptera*. The mulberry-feeding silkworms belong to the family *Bombycidae*, and the other kinds to either the *Saturniidae* or the *Eupterotidae*. The silk of the *Bombycidae* is usually termed 'true silk,' whilst the other varieties are spoken of as 'wild silks.' Those races which complete the life-cycle only once a year are said to be univoltine, whilst those which pass through the cycle more frequently are known as bi-, tri-, quadri-, or multi-voltine. The cocoons of the univoltine varieties are, as a rule, greatly superior to those of the other kinds. Among the wild silkworms may be mentioned: *Attacus ricini*, the Eri variety of India; *A. Cynthia*, the Ailanthus variety of China and India; *Antheraea yama-mai*, the oak-feeding silkworm of Japan; *A. assamensis*, the Muga worm of Assam; *A. mylitta*, the Indian tussah worm; *A. pernyi*, the Chinese tussah worm; and various species of *Anaphe*, the wild silkworms of Africa which form curious nests or aggregations of cocoons.

The fluid which gives rise to the silk fibre is formed in two glands in the body, and is exuded through two ducts or openings in the head of the caterpillar into a common orifice. The viscous streams there become coated with another secretion which flows from two other symmetrically placed glands and thus become cemented together into a double strand. On emerging into the air the fibre coagulates and becomes a firm, continuous filament, the 'bave,' composed of the two parallel strands, each of which is known as a 'brin.' When the young moth emerges from the pupa or chrysalis, it softens the end of the cocoon immediately in front of its head by the emission of a liquid, and then forces its way out. In thus effecting its egress it destroys the continuity of the fibre; in order to obtain the silk of full length, it is, therefore, necessary to kill the chrysalis, and this is accomplished either by steaming the cocoons, submitting them to a dry heat of 70° – 80° , or by freezing them.

A method for killing the chrysalides by chloropicrin is described by Bertrand (*Ann. Inst. Pasteur*, 1924, 38, 529). Satisfactory results have been obtained by its use in small and large scale trials; the process is rapid and the resulting silk excellent in all respects. About 1 grm. of chloropicrin at 22° is sufficient for the treatment of 1 kg. of cocoons (*J. Soc. Chem. Ind.* 1924, 43, B. 741).

The mulberry silkworm (*Bombyx Mori*) is probably indigenous to China, but has been introduced into almost every part of the world in which the mulberry tree (*Morus alba* [Linn.]) can be grown. It yields the best and finest silk in temperate climates, where it is usually univoltine, although sometimes it may be bivoltine. The cocoon consists of an outer, loosely woven fibre, the 'floss,' enclosing an inner, compact portion, the 'pod,' the most internal layer of which consists of a mass of closely agglutinated

fibre forming a hard, gummy husk. The weight of the cocoons varies from 1 to 3 grms. About one-sixth of this is silk, of which about one-half can be unwound or reeled; the other half, consisting of the outer floss and the inner husk, is usually combed or carded, and afterwards spun. Many of the wild silks cannot be reeled at all, and in such cases the whole of the fibre is carded and spun.

The diameter of the raw silk fibre, *i.e.* the double strand or bave, of the mulberry silkworm is about 0.020–0.025 mm., whilst that of the wild silks is usually much greater and varies from 0.040 to 0.065 mm.

Silk is a hygroscopic substance and loses 10–15 p.c. of moisture at 120°. It is a non-conductor of electricity, and is readily electrified by friction; this sometimes renders it difficult to deal with in manufacturing operations, and may necessitate the application of glycerol or soap solution. The fibre is characterised by its exceedingly high lustre and its great strength and elasticity. It is also distinguished by the peculiar sound or 'scroop' it emits when pressed or rubbed, and to which the well-known rustle of silk fabrics is due. The density of raw silk is 1.30–1.37, and that of the degummed fibre is 1.25.

It has been shown by Städeler (Annalen, 1859, 111, 12) that the silk fibre consists of a central core of the protein *fibroin*, coated with another protein, the silk-gum or *sericin*. These substances are accompanied in raw silk by about 1 p.c. of waxy matter, a small quantity of colouring matter, and a variable amount of mineral constituents, ranging from 1 to 5 p.c. The fibroin constitutes about 70–75 p.c., and the sericin 20–25 p.c. of the dry fibre. Before silk is manufactured into textiles, it is heated in a solution of soap at 95° in order to remove the sericin, this process being known as 'boiling off' or 'degumming.' The bave becomes divided in this operation into the separate strands or brins of nearly pure fibroin, which is much softer and more lustrous than the raw material.

Fibroin is insoluble in water and organic solvents, but dissolves in concentrated solutions of alkali hydroxides, in mineral acids, in ammoniacal solutions of cupric oxide and nickel oxide, and in strong solutions of basic zinc chloride.

Sericin is a substance of a gelatinous nature; it dissolves readily in warm soap solution or hot water, and the solution on cooling forms a jelly even when as little as 1 p.c. of the substance is present. On adding alcohol to a hot solution of sericin, the latter is precipitated as a white powder.

These proteins differ from keratin (the protein of wool, hair, &c.) in being free from sulphur. The products of their hydrolysis were first studied by Cramer (J. pr. Chem. 1865, 96, 97), who obtained serine from sericin. Weyl (Ber. 1888, 21, 1407) found that if alcohol is added to a solution of silk-fibroin in cold, concentrated hydrochloric acid, a precipitate is produced which he termed *sericin*. Fischer and Bergell (*ibid.* 1903, 36, 2592) have shown that if fibroin is left in contact with strong hydrochloric acid for about 24 hours, alcohol no longer causes the formation of a precipitate,

and that on evaporating the solution in a vacuum a residue is obtained containing the hydrochloride of a peptone. When this peptone is digested with trypsin it loses tyrosine and becomes converted into glycyl-*D*-alanine. Fischer and Abderhalden (*ibid.* 1907, 30, 574) subsequently isolated another dipeptide, glycyl-*L*-tyrosine, and a tetrapeptide, consisting of two glycine, one alanine and one tyrosine residues; this tetrapeptide, on partial hydrolysis, yielded glycyl-*D*-alanine and glycyl-*L*-tyrosine. Abderhalden (Zeitsch. physiol. Chem. 1911, 72, 1) obtained a tripeptide from the hydrolysis of fibroin, *viz.* *D*-alanyl-glycyl-*L*-tyrosine, which was probably formed from the tetrapeptide. A further study by Abderhalden of the intermediate products of the hydrolysis of silk fibroin has also been recorded (Zeitsch. physiol. Chem. 1922, 120, 207; 1923, 129, 143–156).

Abderhalden and his co-workers have carried out a series of hydrolyses with the object of ascertaining whether the fibroins of different kinds of silk from different sources and from different insects show differences in composition. The results of these investigations are stated in the table given below, the figures representing percentages of dry silk-fibroin after deducting the ash and the non-hydrolysable portion.

Abderhalden (Zeitsch. physiol. Chem. 1911, 74, 427) has shown that Anaphe silk, on hydrolysis, yields a relatively large proportion of tyrosine and considerable quantities of glycine and alanine; aspartic and glutamic acids are also produced, together with traces of leucine and proline. The composition of this silk is therefore similar to that of the other varieties.

It is evident from these results that silk-fibroin is mainly composed of three amino-acid residues, *viz.* those of glycine, alanine, and tyrosine, whilst the other constituent amino-acids are present in relatively small proportions. The fibroins of the various kinds of silk possess a close similarity, but are not identical. Some varieties, such as Italian silk, yield large quantities of glycine, whilst silks of the wild types, such as the tussah silks, give a much smaller proportion of this substance. This has been confirmed by Inouye, Iwaoka, and Hirasawa in the case of Japanese and Manchurian tussah silks (J. Tokyo Chem. Soc. 1920, 41, 876).

An investigation, by X-ray methods, of the physical structure of fibroin from nine different sources, has been made by R. Brill (Annalen, 1923, 434, 204). It is shown that fibroin is a mixture of at least two proteins, of which one is crystalline (the unit silk crystal) and is present in all the samples examined. It appears that the silk protein consists of a compound formed from alanine and glycine in equimolecular proportions, these, as is indicated by the symmetry relationships observed, possibly being united to form a ring, formed of four *D*-alanylglycine anhydride groupings, combined as in a polypeptide (Chem. Soc. Absts. 1924, 126, i. 102).

The hydrolysis of sericin has been studied by Fischer and Skita (Zeitsch. physiol. Chem. 1901, 33, 221), and more recently by Abderhalden and Worms (*ibid.* 1909, 62, 142) and Strauch (*ibid.* 1911, 71, 365), who obtained the following results, which show that the composition of this protein differs greatly from that of fibroin.

HYDROLYSIS OF SILK-FIBROIN.

	From Italian silk (Fischer and Skita, Zeitsch. physiol. Chem. 33, 177)	From New-Chwang silk (Abderhalden and Rilliet, <i>ibid.</i> 1909, 58, 337)	From Canton silk (Abderhalden and Behrend, <i>ibid.</i> 1909, 59, 236)	From Shantung Tussah silk (Abderhalden and Brahm, <i>ibid.</i> 1909, 61, 256)	From Bengal silk (Abderhalden and Singleton, <i>ibid.</i> 1909, 61, 259)	From Niet ngō tsam silk (Abderhalden and Brossa, <i>ibid.</i> 1909, 62, 129)	From Indian Tussah silk (Abderhalden and Spack, <i>ibid.</i> 1909, 62, 131)	From Tsai-tsao-tsam silk (Abderhalden and Schmid, <i>ibid.</i> 1910, 64, 460)	From Chefoo silk (Abderhalden and Welde, <i>ibid.</i> 1910, 64, 462)	From Italian silk (Roose, <i>ibid.</i> 1910, 68, 273)	From Haruko silk (Suwa, <i>ibid.</i> 1910, 68, 275)
Glycine . . .	36.0	19.7	37.5	14.5	30.5	24.0	9.5	25.2	12.5	33.5	35.0
Alanine . . .	21.0	23.8	23.5	22.0	20.0	18.5	24.0	18.2	18.0	20.0	22.6
Leucine . . .	1.5	1.6	1.5	1.0	1.2	1.2	1.5	0.9	1.2	0.75	0.7
Serine . . .	1.6	1.0	1.5	1.8	1.75	1.5	2.0	1.2	1.0	1.9	0.7
Aspartic acid .	present	2.9	0.75	1.0	0.8	2.0	2.5	2.1	2.0	1.0	1.0
Glutamic acid .	nil	1.7	not detected	1.75	trace	3.0	1.0	2.0	2.0	0.25	0.07
Phenylalanine .	1.5	1.2	1.6	1.0	1.4	1.0	0.6	1.0	1.0	1.2	1.3
Tyrosine . . .	10.5	9.8	9.8	9.7	10.0	7.8	9.2	7.8	8.5	9.0	9.7
Proline . . .	present	1.85	1.0	2.5	1.0	1.2	1.0	1.0	2.5	0.8	0.7

Hydrolysis of Sericin or Silk-gum.

	From Canton silk (Abderhalden and Worms).	From Indian Tussah silk (Strauch).
Glycine . . .	1.2	1.5
Alanine . . .	9.2	9.8
Leucine . . .	5.0	4.8
Serine . . .	5.8	5.4
Aspartic acid .	2.5	2.8
Glutamic acid .	2.0	1.8
Phenylalanine .	0.6	0.3
Tyrosine . . .	2.3	1.0
Proline . . .	2.5	3.0

A study of the hydrolysis of the silk of a bivoltine species of silkworm, carried out by Inouye and Hirasawa (Journ. Tokyo Chem. Soc. 1918, 39, 300), has shown that the amino-acids contained in the silk of this species are similar in amount and nature to those of the univoltine species. The sericin separated from the silk of the bivoltine species, however, gave on hydrolysis the following results, which differ considerably from those yielded by the sericin of univoltine silk: glycine 3.9; alanine, 3.5; leucine, 0.4; serine, 5.9; aspartic acid, 3.9; glutamic acid, 0.8; phenylalanine, 0.5; tyrosine, 3.2; proline, 0.4 p.c. The sericin of the bivoltine silk thus has a different constitution from that of the univoltine species, and this corresponds with the fact that the cocoons of the former species can be more easily reeled than those of the latter.

The following method is recommended by Utz for the analysis of silk. A sample of the silk is dried to determine the moisture content, and the sericin is then measured by the loss of weight which occurs when the dried sample is boiled for 70 minutes in 600 c.c. of a 0.75 p.c. solution of olive oil soap, and is afterwards washed three times in 500 c.c. of distilled water and dried at 105°–120°. Fibroin content is determined by boiling 1–2 grams of the sample for 2 hours in a 2.5–3.0 p.c. solution of soap, further boiling it in a solution of sodium

carbonate of 1.5°Bé. (sp.gr. 1.01) until all volatile ammonia is removed, and afterwards estimating the nitrogen in the dried residue by a modification of the Kjeldahl method. The fibroin content is calculated, assuming that 1 part of nitrogen is equivalent to 5.455 parts of pure fibroin. The amount of loading material is obtained by difference. The Kjeldahl process is carried out by heating 0.5–1.0 gram of the treated silk with 20 c.c. of concentrated sulphuric acid, 30 p.c. hydrogen peroxide (nitrogen free) being occasionally added in portions of 1 c.c. until the reaction mixture is colourless. The time required for complete decomposition of the silk is thus reduced from 4–6 hours to 20 minutes (Chem. Zeit. 1923, 47, 36; J. Soc. Chem. Ind. 1923, 177, A).

For further information on silk reference should be made to Matthews' Textile Fibres.

E. G.

SILK, ARTIFICIAL (or RAYON). These products are in practice prepared from solutions of organic colloids such as cellulose, and for the chemistry of their preparation reference be made to the general article on CELLULOSE in Vol. I.

History.—In 1734 Réaumur suggested the manufacture of filaments to take the place of those produced by the silkworm. In 1855 Andermars actually patented the production of such threads or filaments from a solution of nitrocellulose (Eng. Pat. 283, 1855). A steel point was dipped into the solution, and a thread drawn from the liquid. The thread was connected with a winding machine by which it was drawn out until the liquid was exhausted.

In 1882 Weston claimed the denitration of nitrocellulose, using such reagents as ammonium sulphide for that purpose (Eng. Pat. 4458, 1882).

In 1883 J. W. Swan (Eng. Pat. 5978, 1883) prepared filaments by squirting a solution of nitrocellulose into 70 p.c. alcohol and denitrating the resulting filaments by means of ammonium sulphide.

In 1884 the first workable process was pro-

tected by de Chardonnet (Fr. Pat. 165349). The apparatus as originally used is shown in a photograph published in a book by Filtzer in 1903.

In this process jets are used, the solution being forced through them at great pressure into warm air. Fine filaments may be drawn off under these circumstances and the solvent (alcohol-ether) partly recovered from the air.

Du Vivier in 1889 produced a product which was practically identical with that of de Chardonnet. In 1892 Lehmer also patented certain modifications, and claimed to be able to work with much lower pressure at the jets (Fr. Pat. 221901).

As the result of these investigations yarns made in this manner came into the market and were used for the production of braids, &c., and at Besançon in France, Tubize in Belgium, and in Germany, Switzerland, and Hungary, this product was manufactured in increasing quantities. An attempt to work this process in this country failed.

Since that time many improvements in the manufacture of filaments by this process have been devised, and some of them patented.

These have been connected with the solution of nitrocellulose, the formation of the threads, subsequent denitration which is necessary to render the yarn less inflammable, the recovery of the solvent, and in other details. The filaments as spun are combined together into threads of a suitable size, and 'thrown' or spun in order that the threads may act properly in the subsequent working.

These yarns or threads resemble in many ways silk. They are extremely lustrous, and in some ways have been considered to be superior to the real article. They are inferior in strength and lack 'covering power,' as a result of which they have a lower value when woven into fabrics. In the manufacture of braids, trimming, &c., this defect is not noticed, or is counterbalanced by the special effects produced.

Chardonnet silk filaments have a mean diameter of $35/\mu$, a true elasticity of 4-5 p.c., a percentage elongation under breaking strain of 15-17 p.c., and a sp.gr. 1.49.

The effect of denitration on the strength of the filaments has been given as follows—

Nature of filament	Breaking Strain	Elasticity
100 denier nitrocellulose thread .	150 grms.	23 p.c.
„ after denitration .	110 grms.	8 „
„ in wet state .	25 grms.	—
Real silk	300 grms.	18 p.c.

According to Dulitz (Chem. Zeit. 1910, 34, 989) it is impossible to completely denitrate the threads without a virtual destruction of their qualities. In practice it is arranged that the yarn contains about 0.05 p.c. nitrogen, but this must be equally distributed over the fibre. To obtain this result many factors in the manufacture of the silk itself have to be considered. These include uniformity of composition, percentage of moisture, and a uniform shrinkage on drying. When hyposulphides are used a new bath is more active than an old one. Many other details have not been disclosed.

The actual process is a difficult one to control. The temperature of the bath has a great effect on the result. This process, which when

properly conducted hardly decreases the lustre of the thread, is followed by a bleaching bath. When finally finished the product possesses a beauty and gloss which has hardly been equalled by other and more recent makes, and probably accounts for the fact that it has survived and is in use at the present time.

This original process of manufacture has since had to compete with others working in a more direct manner, in which the cellulose itself is dissolved, and the nitration and denitration processes dispensed with. The solvents are more easily handled and are cheaper to use. Aqueous solutions have taken the place of air as a medium for filament formation, coagulation of the colloid replacing the evaporation of the solvent. In some cases these act chemically on the solvents in such a way that the cellulose is thrown out of solution.

Dealing with the more important of these recent processes, in their historical sequence, Wynn and Powell, in 1884 (Eng. Pat. 16805, 1884), used a solution of zinc chloride as a solvent for cellulose. This solution was expressed into a solution—say alcohol—which removed the solvent. The cellulose was precipitated in the form of gelatinous filaments which could, under certain conditions of manufacture, be collected, and after further treatment, dried.

These have been greatly used in the past for the production of filaments for carbon lamps. Modifications in this process were proposed by Dreaper and Tompkins (Eng. Pats. 10487, 17901, of 1897), and by Bronnert respectively; the former first claimed the process of obtaining lustrous filaments by drying under high tension, a process which has since been universally employed in viscose and cuproammonium works, but for certain reasons this zinc chloride process has never been used on any scale for the production of filaments for textile purposes.

Six years after Wynn and Powell had filed their specification Despaissis (Fr. Pat. 203741, 1890) provisionally protected a process in which the cellulose was dissolved in an ammoniacal solution of copper, and then squirted into a solution which would, by acting chemically, precipitate the cellulose in the required manner. Owing to the death of the inventor the patent was never completed and published. A patent on almost identical lines was taken out in 1897 by Pauly. Many others have followed dealing with important details in the manufacture, variations in the solutions used for precipitation, use of special copper salts such as copper carbonate, in detail in the machinery used, and special treatment of the threads produced, but many essential details of manufacture have not been published.

It is difficult to state the relative value of the different suggestions. Generally speaking, the solutions used to precipitate the cellulose are either acid or alkaline in their nature. The addition of substances like dextrose has been suggested to facilitate working conditions. The cellulose has been treated before solution with caustic soda to facilitate the process. Fremery and Urban have suggested many modifications which deal with the treatment of the threads after formation, and in the subsequent drying operations.

The third process, which is at present meeting with particular success, entails the use of cellulose

thiocarbonates, which were discovered in 1892 by Cross, Bevan and Beadle. By spontaneous decomposition cellulose is regenerated from such a solution and thrown out in an insoluble condition. This process may take place rapidly in the presence of suitable salts; and in 1903 Stearn (Eng. Pat. 1020, 1898) disclosed a commercial method of preparing filaments from this solution, using a solution of an ammonium salt as a precipitating medium.

Many patents have since been taken out in connection with this process, but here again much remains unpublished. The use of bisulphate of sodium in the precipitating solution by Muller marked a distinct advance in the manufacture. The addition of glucose to the same solution in conjunction with a mineral acid (Courtauld and Wilson) and the use of glucose with sodium or ammonium sulphate and sulphuric acid with 1 p.c. of a zinc salt (Courtauld and Napper) have also played a part in the development of the viscose process. Recently finer filaments have been prepared by the viscose method which still accounts for a large proportion of the world's output, and (Cross) an industrial capitalisation of £100,000,000.

Recently processes have been developed by Bronnert (Eng. Pat. 170024) and Dreaper (Eng. Pat. 215028) respectively for the production of fine filament viscose yarns.

Attempts have been made to manufacture filaments from cellulose esters such as the acetates or formates. The former substance presents as a raw material advantages, but the high cost of manufacture and difficulties in the matter of solution, and the subsequent reprecipitation in the required form are considerable. The substance is water-resisting, and special conditions have to be observed in dyeing these filaments.

Cellulose acetate filaments are prepared in this country on a large scale, it now being possible to dye the product; which is also less brittle than formerly. Until the selling price of artificial silk reaches a normal figure, and the world's demand is reasonably satisfied, it is difficult to determine the relative economic value of this product in comparison with the viscose one.

A cellulose acetate product has been tested by Herzog (Chem. Zeit. 1910, 34, 347). The average diameter equals 42.3μ .

It is soluble in cold acetic acid, coloured yellow by sulphuric acid, and iodine, and also by zinc chloride and iodine. It does not swell in water, and has a low density, viz. 1.251.

Filaments and threads have also been prepared from gelatin and casein, but little has been heard of their production on a commercial scale.

Directly connected with the manufacture of these yarns is the question of the recovery of the solvents used, and also of the materials used for precipitation. In some processes this may even be an essential condition to commercial success.

Reference to many patents will indicate that the machinery used in the different processes varies greatly, and is in some cases of a complicated nature. Mention might here be made of the patents dealing with the production of very fine filaments, as proposed by Thiele, where conditions of working are such that these filaments can be prepared commercially.

Machinery.—Each process has its specific requirements as regards machinery employed, and this varies considerably in detail even in works manufacturing the same final product. The same process working in different countries differs materially in actual methods. There is also a mass of detail, which in many cases is not protected in any other way than that of secret working, and this may in cases be confined to the working of a single factory. One or two cases which illustrate the methods adopted in the manufacture of these threads may be considered.

The first case is that of the original Chardonnet apparatus. This is of interest as showing in the original patent (Eng. Pat. 2211, 1886) the apparatus already available at that time. The thread passed through a jet, which had a bore of $\frac{1}{20}$ – $\frac{1}{5}$ mm., through a very short column of water and then on to the winder. When a thread broke, the broken end was seized by pincers and carried over guides to the reel to be wound. The pinions still ascending are cleaned by a rapidly revolving brush, before they descend again to pick up any more broken ends. This movement was repeated several times a minute. Air heated to 85°–90°F. is passed by supply and discharge conduits through the outer chamber. The volatile solvents carried off by the air might be 'condensed and removed by cooling,' and the air after warming returned to the apparatus. The Topham turbine system of collecting and spinning the threads at the same time (Eng. Pat. 23158, 1900) is a good illustration of the methods adopted to overcome certain difficulties in manipulation. The squirted thread passes over a roller and thence into a rapidly rotating box. The fibres or threads as they are fed in are twisted together and caused by the centrifugal force to form a compact coil around the interior of the box which when removed form hanks or skeins. If the boxes are deep, a longitudinal reciprocating movement can be given to either the box or the funnel to make sure of the even coiling of the thread in the skein form. This is an ingenious method of combining the skeining and twisting in one operation. It has been largely used in the manufacture of artificial silk, as it reduces the strain on the newly formed threads to a minimum.

A third example is that of a patent dealing with modifications in the Thiele 'two-solution' process of spinning (Dreaper, Eng. Pat. 21872, 1908). In this case arrangements are made so that the freshly squirted thread comes in contact with a precipitating solution which acts comparatively slowly, and then passes into a stronger one, which is contained in a second tube. The solution of cellulose flows through a delivery pipe to a composite jet. The weaker solution enters the inner tube and the stronger one the outer one which is attached to a vacuum pump which may be used in filling the tubes with solution in the first place. The threads, after this double treatment, pass out at the lower end of the outer and longer tube, and are wound on to suitable bobbins or otherwise treated. These examples may be taken as illustrating the different methods in vogue. For further details the patent literature of the last fifteen years should be consulted.

The fibres generally have specific properties which have made them useful in commerce. The extreme brightness of the yarns, which may, if required, exceed that of real silk, is probably the most important quality in the coarser threads. The ash is generally under 2 p.c., and the nitrogen varies between 0.05 and 0.13 p.c.

Strangely enough the latter refers to a 'direct' process, and the former to a nitro-cellulose one. Silk contains 17 p.c. of nitrogen, so that in this way it is distinguished from the artificial silk products derived from cellulose, but not from those which may be derived from proteids, such as casein, gelatin, &c.

Identification of Artificial Silks. The following simple chemical tests are described for distinguishing between the various commercial artificial silks: A small tuft of the silk is heated in a dry tube, and the vapours are tested with litmus paper. Alkaline vapours indicate gelatin silk, and acid vapours silks of cellulose basis. With iodine-zinc chloride and iodine-sulphuric acid, the reagents being made at suitable concentration, cellulose acetate silk is stained yellow, and the cellulose silks reddish-violet or blue. In cold concentrated sulphuric acid the collodion and viscose cellulose silks dissolve rapidly, cuprammonium silks only slowly. In warm 40 p.c. caustic potash solution the cellulose and cellulose acetate silks are swollen, while gelatin silk dissolves rapidly and completely. In cuprammonium reagent the cellulose silks swell and dissolve, cellulose acetate silk swells without dissolving, and gelatin silk takes a bluish-violet coloration without dissolving. The nickel-oxide-ammonia reagent, both cold and warm, causes swelling of the cellulose and cellulose acetate silks without dissolving; gelatin silk takes a brown coloration without dissolving. Alkaline copper glycerol solution has no action on the cellulose and cellulose acetate silks on boiling, but gelatine silk dissolves in a short time. Diphenylamine-sulphuric acid gives a blue coloration with collodion silk, and serves to distinguish this from the other varieties of cellulose silk. Dyed samples should be 'stripped' by means of hydrosulphite before applying the reagents. The tests should be controlled by comparison with type samples of known origin (L. J. Matos, Chem. Engineer, 1914, 20, 209; Analyst, 1915, 66).

Formhals (Chem. Zeit. 1919, 43, 386) gives the following method: a small portion of the sample is treated for a short time with a few c.c. of concentrated sulphuric acid, the mixture is diluted with water, the solution rendered alkaline with sodium hydroxide, and diazotised *p*-nitraniline solution is added. Under these conditions, natural silk gives a red solution and artificial silk a yellow solution. The test may be applied to weighted and dyed silks (J. Soc. Chem. Ind. 1919, 624, A).

The method of detecting the origin of such products depends upon certain chemical tests. The diphenylamine one has generally been used in the past, and a solution of the sulphate may give the following reactions:—

Silk	Brown coloration
Tussah silk (wild)	„ but more intense
Nitrocellulose products	Intense blue
Viscose and cupram-	
monium products	No reaction.

Schwalbe's test with Barreswil's (Fehling) solution and one with a solution of iodine in zinc chloride are not so satisfactory. The relative action with dye-stuffs is of little account in this direction.

Maschner proposes to make use of the action of concentrated sulphuric acid in the following way. 0.2 grm. of the different qualities are introduced into small Erlenmeyer flasks, which stand on white paper, and equal amounts of pure sulphuric acid, 10 c.c., are simultaneously poured over them, and the fibres thoroughly moistened by shaking. A nitrocellulose silk remains colourless, after 40–60 mins., the solution takes a pale-yellow tinge. Cuprammonium silk at once turns yellow, or yellowish-brown; the solution is yellowish-brown after 40–60 mins. Viscose silk at once turns reddish-brown, and after 40–60 mins. the solution is a rusty-brown colour.

A nitrocellulose product should show no carbonising when heated to 135°–140°. The presence of cellulose sulphuric esters which may not be removed in the denitration process may cause a complete loss of strength owing to the slow production of free sulphuric acid.

A physical method of differentiation between artificial and natural silks based on the differences between the refractive indices, and which is applicable to the case of dyed fabrics, is described by Herzog (Zeitsch. angew. Chem. 1918, 31; Ref. 225, J. Soc. Chem. Ind. 1918, 574, A). A fibre of natural silk mounted in aniline and examined under a microscope with a nicol prism is almost invisible when its longitudinal axis is at right angles to the plane of polarisation of the prism, and becomes more and more visible when the stage is rotated, until it reaches a maximum of visibility at right angles to the original position. Artificial silk fibres have a refractive index considerably below that of aniline and are distinctly visible at all positions of the revolving stage.

The specific gravity of the different products when compared with real silk or cellulose is as follows:—

Chardonnet	1.52
Lehner	1.51
Glanzstoff	1.50
Cellulose acetate	1.251
Natural silk	1.36
Cellulose	1.45

The normal moisture present has been given as follows: real silk, 10–11 p.c.; Chardonnet, 10.37 p.c.; Lehner, 10.71 p.c.; Glanzstoff, 10.04 p.c.

The loss of strength on wetting has been a drawback to the use of such materials in certain fabrics. It must be remembered, however, that this defect is of a temporary nature, as the strength is regained on drying. This defect is gradually decreasing, and may in time be overcome. A considerable improvement has taken place since Strehlenert, in 1904, published the following figures:—

Yarn	Dry strength	Wet strength	P.c. loss
China silk	53.2	46.7	14.1
French (ecrue)	50.4	40.9	18.8
Chardonnet	14.7	1.7	89.6
Lehner silk	17.1	4.3	74.8
Viscose	31.5	3.5	84.0
Glanzstoff	19.1	3.2	83.0

These figures show an average loss for artificial products of 82 p.c., and for real silk of 16.4 p.c. This loss in the former case has now fallen to about 50–60 p.c. or even less. The relative wearing properties of different yarns do not necessarily depend upon their strength and elasticity, as this is indicated on the ordinary testing machine. This condition also applies

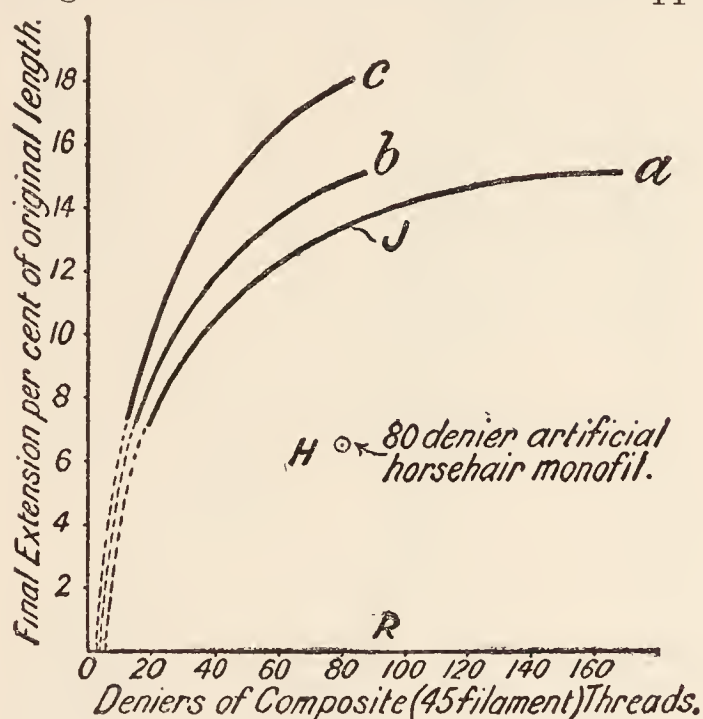


FIG. 1.

to the relative value of two yarns which vary in their loss of strength on wetting.

The influence of variations in the actual size of the filaments making up the artificial silk threads on the final extension at breaking, and the breaking stress is shown in the diagrams.

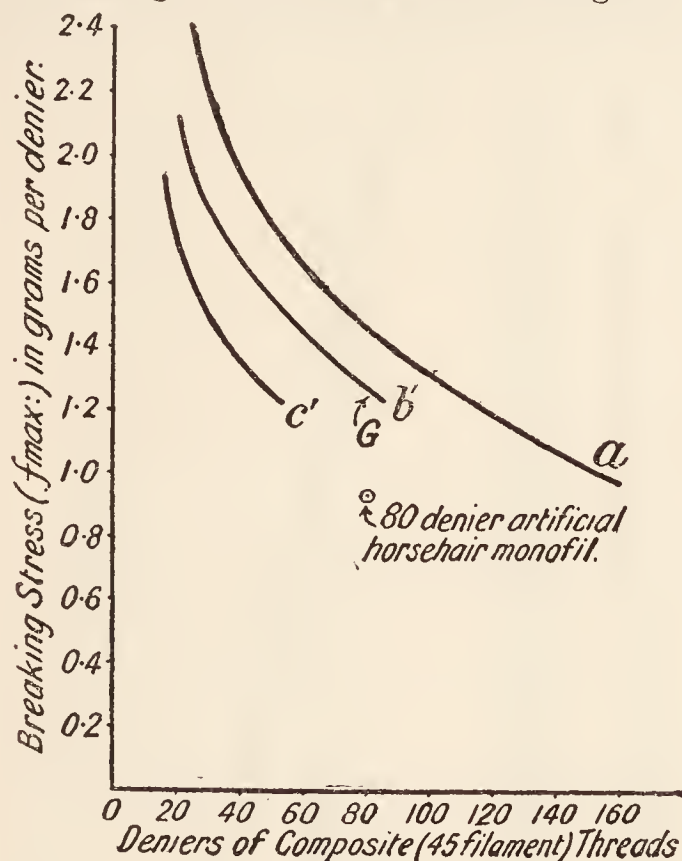


FIG. 2.

The general strength of these filaments is stated in grams per denier; but, as Dreaper and Davis (J. Soc. Chem. Ind. 1909, 28, 1300) have shown, this is not an entirely satisfactory manner of stating the relative strength, unless the size of the individual filaments is constant or accurately known.

Figs. 1 and 2, taken from the above communication, indicate the final extension before breaking, and the actual breaking stress of artificial threads of varying size.

Fig. 3 shows typical load-extension curves obtained with single filaments of large diameter (artificial horse-hair). The normal stress at fracture for a 200 denier thread is 49,000 lbs. per square inch, and the percentage extension is 20 p.c. It is observed that the curves in this case are characteristic of those obtained with metal wires.

Cross and Bevan have given the strength of coarse count silks as between 1.0 and 1.4 grms. per denier for artificial products, as against 2.0 and 2.5 grms. per denier for the real product. But in the counts containing finer filaments this may be exceeded in the former case. The term 'elasticity' as applied to these filaments in a composite thread is not valid, as other factors, such as the rearrangement of the filaments under strain, also enter into this figure. A practical trial is necessary before the value of any individual product can be obtained from the point of view of weaving or actual wear. In

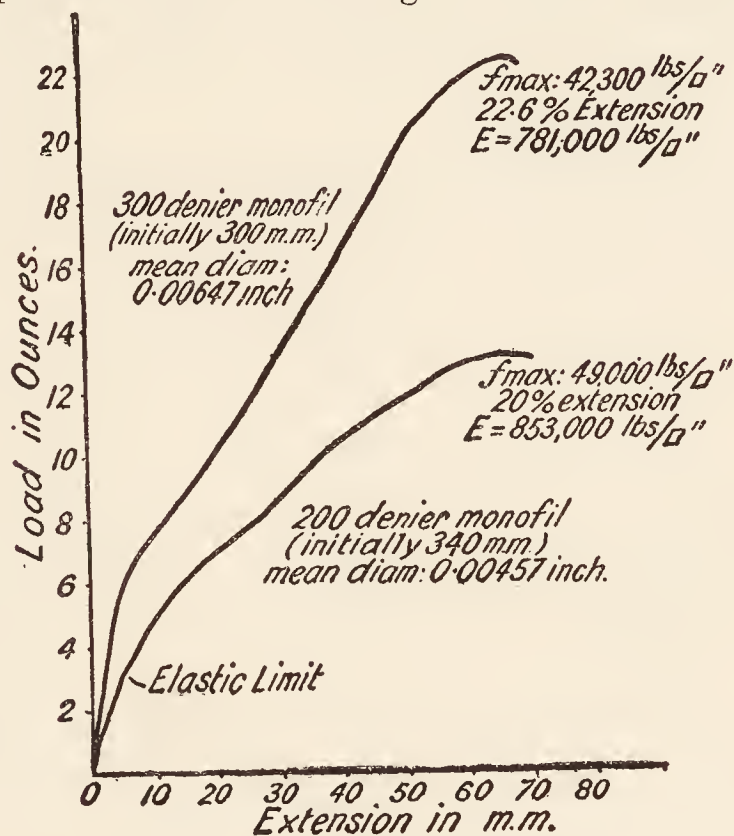


FIG. 3.

calculating the size of such threads, 900 metres of thread of a weight of 0.1 grm. = 1 denier, and so on.

The size of the actual filaments making up the threads is a matter of considerable importance. If they are of large diameter the silk may have a harsh feel, but it will probably be very brilliant. When threads are required for weaving purposes the filaments are generally of less diameter. This also gives softness and increased strength. It is possible to spin such filaments much finer than those of natural silk.

The relative diameter of the filaments at present on the market varies not only with the different makes, but according to the requirements and uses to which the yarns are put. The following figures represent the variations noticed in certain cases—

Nature of materials	Size in microns
Chardonnnet	35–100
Lehner	40–132
Pauly	40–70
Viscose	10–60
Thiele	7–15
Cellulose acetate	10–60
Gelatin	60–85
Real silk	10–15

(A micron = 0.001 mm.)

Many attempts have been made to improve the water-resisting qualities of these products. A method put forward is known as the Sthénose treatment. The silk is subjected to the action of formaldehyde, which, according to Escalier, leads to a condensation of the cellulose molecule and gives greater strength in both the dry and wet state, but specially in the latter.

Quality	Size	Tenacity (wet)	Tenacity (dry)
Sthénose .	130 den.	208	140
Viscose .	130	146	38
Givet .	120	130	39.5
Chardonnet .	90	144	39.6

These figures certainly indicate an increase in strength as present both in the dry and wet state after this treatment, but certain difficulties have been experienced in the past in dyeing these filaments and threads. Different makes of artificial silk react in varying ways in this respect. The nitrocellulose product will not stand so severe a bleaching as the ordinary cellulose products.

Special colour effects may be obtained by taking advantage of the different dyeing properties of these materials as compared with natural fibres, or even different artificial ones, when they are present together in fabrics.

The 'feel' of these yarns is improved by a passage through a weak acid bath as in the case of silk.

De Chardonnet (Compt. rend. 1918, 167, 489; J. Soc. Chem. Ind. 1918, 650, A) has drawn attention to the fact that the cross-sectional contours of artificial silks are a characteristic indication of the physical conditions of spinning, and therefore a useful guide in the identification of origin.

The world's output of these yarns has been variously estimated. The output of real silk in time of peace is about 60,000 tons. The output of the artificial product is continually increasing, especially as some of the products are now being used in large quantities in the weaving of fabrics. The world's production to-day is at the rate of 90,000 tons per annum, of which probably 85 p.c. is made by the viscose process. It is difficult to obtain figures giving the relative output of these yarns as made by the different processes in vogue, but the output of the nitrocellulose product has rapidly decreased, and that of the viscose product has greatly increased. The future of the cupro-ammonium process will depend upon certain factors which are closely connected with the production of fine filaments.

Figs. 4 and 5 illustrate the relative nature of certain fine and coarse count artificial fibres enlarged to 80 diameters.

A recent extension of this industry is seen in the production of 'staple fibre' which consists of a number of filaments of from 2 to 10 in. in length. This is spun either alone, or in admixture with other fibres. The output of the product is already 100 tons per day, and in time is likely to exceed that of artificial silk.

References.—Nitrocellulose Industry, vol. i. 1911, by Worden; Die Künstliche Seide, by Suvern; Fabrikation de la soie artificielle, by T. Foltzer; Matthews, Textile Colourist, 27, 322; Dreaper, J. Soc. Dyers. 1907, 23, 7; J. Soc.

Chem. Ind. 1909, 28, 1300; E. Berl., Chemiker Zeitung, 1910, 34, 532; Singer, J. Soc. Dyers. 1914, 30, 182; Wilson, J. Soc. Chem. Ind. 1917, 36, 817; and many other references which may



FIG. 4.—Thiele product.

be found in Worden's 'Nitrocellulose Industry,' vol. i. 1911, or in the patent literature. On the dyeing of artificial silk, see Wilson and Imison,



FIG. 5.—Viscose product.

J. Soc. Chem. Ind. 1920, 39, 322, T; Green and Sanders, J. Soc. Dyers, 1923, 39, 10. On the analysis, see Die Unterscheidung der natürlichen und Künstlichen Seiden, by Herzog; and

Allen's Organic Analysis, vol. viii. (Dreaper), 645 *et seq.*

Statistics are appended showing the world production in 1922, according to an estimate prepared by the American Viscose Co., revised figures calculated by the Bulletin des Soies et des Soieries, of Lyons, on the basis of the daily output given in parentheses :

	Kgs.
United States .	10,645,500
England .	6,949,020 (2,038,500)
Germany .	5,700,552 (4,756,500)
Belgium .	2,850,276 (3,397,500)
France .	2,850,276 (4,077,000)
Italy .	2,850,276 (2,718,000)
Holland .	1,140,110 (543,600)
Switzerland .	855,052 (2,718,000)
Hungary .	855,082
Austria .	712,569
Poland .	427,541 (271,800)
Czechoslovakia	285,027
<hr/>	
	36,121,284 (18,060 tons)

(Journ. Soc. Chem. Ind. 1923, 42, 748.)

The production of artificial silk in the United States during 1922 was 24,406,000 lbs., as compared with 15,000,000 lbs. in 1921, 5,828,000 lbs. in 1918, and 1,566,000 lbs. in 1913. Figures are not available for the imports of artificial silk in 1922, but it is believed that the amount is less than in 1921, when 3,667,180 lbs. was imported (Ch. Comm. J. April 27, 1923; *cf.* J. Soc. Chem. Ind. 1923, 42, 455).

In 1913 the production of artificial silk was estimated at 9,000 tons, and 1922 at 31,000 to 32,000 tons. The 1923 figures are uncertain, estimates ranging from 31,200 to 42,000 tons.

The world's output of these yarns in 1925 is estimated as follows:—

Country.	Metric tons per annum.
U.S.A. .	25,000
England .	15,000
Germany .	12,000
Italy .	20,000
France .	7,000
Belgium .	6,000
Switzerland .	3,000
Holland .	3,000
Austria .	2,000
Poland .	1,500
Czecho-Slovakia	1,000
Japan .	1,500
Hungary .	500
Spain .	200
Sweden .	80
Russia .	40
<hr/>	
Total .	97,820

It is estimated that in the year 1927 the output will exceed 150,000 tons, and then gradually increase to a minimum output of 600,000 tons per annum, when the output of artificially produced filaments will be roughly ten times that of the production of natural silk yarns, and compare with the 7,200,000 tons of wool produced per annum.

Natural silk production is confined to those countries where the silk worm can thrive, but

artificial silk manufacture is almost independent of consideration of raw materials, and thus becomes established where the demand exists. The largest market is found in the United States, which besides producing one third of the world's total output also imports further supplies. The largest exports of artificial silk are made from Belgium and Italy. W. P. D.

SILK GREEN. *Chrome green v.* CHROMIUM.

SILLIMANITE or **FIBROLITE.** The aluminium silicate Al_2SiO_5 or $\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ is the only known anhydrous compound of silica and alumina. This is trimorphous and is known in nature as the following three minerals:—

Al_2SiO_5	{ Andalusite, orthorhombic, sp.gr. 3.18
	{ Sillimanite, orthorhombic „ 3.25
	{ Kyanite, triclinic . „ 3.66

Sillimanite is the most stable form, and the only one that has been produced artificially. Both kyanite and andalusite are transformed into sillimanite at 1350° with evolution of heat; m.p. about 1816° . Kyanite (*q.v.*) differs markedly in its physical characters, but between andalusite (*q.v.*) and sillimanite the difference is not so great, as shown by the following data:—

	Sillimanite	Andalusite
Axial ratios		
$a : b : c$.	0.97 : 1 : 1.34	0.9861 : 1 : 0.7024
Prism angle (110) \wedge (110)	$88^\circ 28'$	$89^\circ 12'$
Cleavage .	$b(010)$ perfect	$m(110)$ distinct
Optic axial plane .	$\parallel b(010)$	$\parallel b(010)$
Acute bisectrix .	$C \perp c(001)$	$A \perp c(001)$
Optical sign .	positive	negative
α_{Na} .	1.6584 *	1.6326
β_{Na} .	1.6596	1.6390
γ_{Na} .	1.6789	1.6440
Hardness .	$7\frac{1}{2}$	$7\frac{1}{2}$

* Refractive indices of artificial sillimanite, $\alpha = 1.638$, $\beta = 1.642$, $\gamma = 1.653$.

Sillimanite occurs as a constituent of certain crystalline schists and metamorphic rocks, in which it is sometimes associated with corundum. It usually forms tough masses with a finely fibrous, more or less matted structure and a light greyish colour. Such material was known in 1792 as Faserkiesel, and in 1802 as fibrolite. The name sillimanite was applied in 1824 to the rarer crystallised material, found as long slender colourless needles in Connecticut. The compact fibrous material has much the appearance of calcined jade; and neolithic stone axes made of it have been found in France and Spain. Translucent material with a silky-lustre is sometimes fashioned as knife-handles and small ornamental objects. Clear material of a pale sapphire-blue colour and of gem quality has been found in Burma and Ceylon (L. J. Spencer, Min. Mag. 1920, 19, 107). In the artificial form, sillimanite is of technical importance as the main constituent of porcelain. This was established by V. I. Vernadsky (1889 and 1890), who obtained crystals by fusing $\text{Al}_2\text{O}_3 + \text{SiO}_2$, or more readily with the mixture $\text{Al}_2\text{O}_3 + 2\text{SiO}_2$. In the latter case the crystals are set in an amorphous base, from which they can be isolated by the action of cold hydrofluoric acid. Crystalline glazes containing needles of sillimanite have been obtained by fusing kaolin with pyrites or ferrous sulphate.

J. Morozewicz (1898) obtained crystals in silicate fusions $\text{RO} \cdot \text{Al}_2\text{O}_3 \cdot n\text{SiO}_2$ when $n > 6$. On account of its very high melting-point, sillimanite is of value as a refractory material. It has been prepared artificially by smelting aluminous rocks or minerals in a cupola furnace with coke. The excess of silica is volatilised as silicon and condenses as a snow-white deposit of silica. If cryolite be present volatilisation of the silica is very rapid. Iron and titanium are helpful, but lime retards the formation of sillimanite. Felspar and mica facilitate the conversion into sillimanite above 1300° , by dissolving the clay, sillimanite crystallising out of the fused solution. After 5 or 6 hours the process is complete, and air is blown through the mass in order to produce cells resembling diatomaceous earth. After cooling, the mass is crushed and iron separated magnetically. This crude sillimanite has sp.gr. 2.62–2.68, and m.p. 1790° – 1920° , and consists of interlacing crystals 0.01 to 0.5 mm. in length with a little amorphous aluminium silicate and slag. It is highly refractory, and free from expansion and contraction at all temperatures. Larger crystals as fibrous masses can also be obtained (A. Malinovsky, J. Amer. Ceramic Soc., 1920, 3, 40; Trans. English Ceramic Soc. 1920, 19, 140). On the artificial production, see also E. S. Shepherd and G. A. Rankin, Amer. J. Sci. 1909, 28, 293.

Mullite. In the system silica-alumina, $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ is the only compound stable at high temperatures, and should therefore be found in rocks of the appropriate composition when formed at high temperatures. An examination of buchites from the island of Mull disclosed that the so-called sillimanite present was really the above compound, and the name, mullite, is therefore proposed for this mineral. The optical properties of mullite are very similar to those of sillimanite; both are orthorhombic, but the mullite prism angle is $89^\circ 13'$ compared with $88^\circ 15'$ for sillimanite, and its refractive indices are lower. Mullite is found in the crowns of glass-pots that have been in use for long periods at high temperatures (Bowen, Greig, and Zies, J. Washington Acad. Sci. 1924, 14, 183; Chem. Soc. Abstr. 1924, 126, ii. 416). L. J. S.

SILOXICON. A by-product obtained in the manufacture of carborundum, consisting mainly of a substance of the formula $\text{Si}_2\text{C}_2\text{O}$, *v.* SILICON.

SILUMIN. An alloy of 11–14 p.c. of silicon and 89–86 p.c. of aluminium. Its sp.gr. is 2.5–2.65, tensile strength 20 kg. per sq. mm., hardness at ordinary temperature 60 kgs. per sq. mm., and at 350° 20–25 kgs. per sq. mm. (with a 500-kg. load and a 10-mm. ball). The alloy is not attacked by wet steam, and is more resistant to dilute acids and concentrated nitric acid than aluminium, which it otherwise resembles chemically.

SILUNDUM is an electric furnace product obtained by the action of silicon vapour or a mixture of silicon vapour and carbon monoxide on carbon. Up to about 1800° a greenish slate-coloured variety of the composition $\text{Si}_4\text{C}_4\text{O}$ is formed. Above 1800° the product is a steel-grey substance, SiC , which is a form of carborundum. At still higher temperatures it is decomposed, forming graphite. Silundum is a good conductor of electricity, and has a negative

temperature coefficient of resistance: at 25° it is 0.1543 ohm per c.c. for the slate-green variety, and 0.2374 ohm for the steel-grey variety. Hardness about 9 on Mohs' scale: sp.gr. 2.9–3.0. Unattacked by acids, or by hydrogen, oxygen, or nitrogen, even at 1100° . Decomposed by fused alkali carbonates and hydroxides in presence of air and by sodium peroxide and lead oxide, but not by fused sodium silicate, borax, potassium bisulphate, cryolite, potassium bichromate, or a mixture of potassium chlorate and nitrate (Tucker and Lowy, J. Ind. Eng. Chem. 1915, 7, 565).

SILVER. Sym. Ag (*Argentum*). At.wt. 107.88. According to Aston, silver has two isotopes of masses 107 and 109. The knowledge of this metal dates from remote antiquity, and the earliest records refer to its use as a medium of exchange. The first mention of silver as a metal appears to have been made about 4500 B.C.

Properties.—In colour silver is whiter than any other common metal or alloy, and it is capable of receiving a brilliant polish. When in the form of fine powder, as, for instance, when the chloride has been reduced by iron and acid, silver is grey and earthy in appearance. A thin film of silver is blue by transmitted light. It crystallises in the cubic system and small octahedra are occasionally observed. The tenacity of silver wire of 1 square mm. in sectional area is equivalent to 17.27 tons per square inch at 0° . It is more malleable and ductile than any other metal except gold, and may be hammered into leaves 0.0025 mm. thick. It is hardened by hammering or rolling, but its softness is restored by annealing at about 200°C . It is harder than gold but softer than copper. It is the most perfect conductor of heat and electricity known, and has therefore been adopted as the standard for comparison. Its conductivity is increased by annealing. Its sp.gr. after having been cast is 10.50, and this is only slightly altered by rolling or annealing. Solid castings of pure silver are, however, difficult to prepare, and a cast ingot usually contains minute cavities by which its density is apparently reduced. Cast silver shows numerous twinned crystals which are revealed by heating in a vacuum, and almost invariably contain small quantities of oxygen and carbon monoxide. Röntgen ray analysis of the structure of silver crystals shows that the atoms are arranged according to the simple face-centred lattice which is identical with the arrangement found by Bragg for crystals of copper (Vegard, Phil. Mag. 1916, [vi.] 31, 83). At temperatures above 570° silver suffers a gradual change in internal structure, which can be demonstrated by photomicrographs. At 800° the elements of a cellular structure begin to appear, and large crystals are formed at 870° (Kahanowicz, Atti R. Accad. Lincei, 31, i. 313). The sp.gr. of molten silver is 9.653 at 1000° , 9.633 at 1025° , and 9.613 at 1050° (Hoffmann and Stahl). Precipitated silver has a density as high as 10.61.

For the specific heats of silver at high temperatures, see Eastmann, Williams and Young (Am. Chem. Soc. J. 46, p. 1178, May 1924; Sci. Abstr. 1924, 27, 748). For the variation with temperature of the atomic condensation (molecular complexity) of antimony, gold and

silver, *see* Jouniaux (Bull. Soc. Chim. 1924, [iv.] 35, 463; Chem Soc. Abstr. 1924, ii. 452).

Silver melts at 961.5° (Holborn and Day), 960.5° (Dana and Foote), and begins to volatilise in a sensible degree at about the m.p. of copper, 1083° . It can be distilled in quantity by the oxyhydrogen blowpipe in a suitable furnace, and boils at 1950° in the electric arc furnace. Its vapour is pale blue. Molten silver absorbs about 22 volumes of oxygen, and the whole of the gas, except 0.7 volume, is given off again during solidification. The disengagement of the gas causes effervescence and 'sprouting,' which may be prevented by the presence of oxidisable metals or by slow cooling. *Cf.* Sieverts and Hagenacker, *Zeitsch. physikal. Chem.* 1909, 68, 115; Donnan and Shaw, *J. Soc. Chem. Ind.* 1910, 29, 987. Troost found (*Compt. rend.* 1884, 93, 1427) that at 778° oxygen and air diffused through silver. Sieverts showed that hydrogen, oxygen, and nitrogen do not diffuse through silver at 640° . According to Spencer (*Chem. Soc. Trans.* 1923, 123, 2124), the rate of diffusion is proportional to the sq. root of the pressure of oxygen, and consequently that the oxygen in silver is in the atomic and not in the molecular form. In the case of air the diffusion is preferential, the nitrogen being held back.

Silver is not acted on by oxygen, whether dry or moist, except to a very slight extent at high temperatures. Chlorine is absorbed by it even at the ordinary temperature with the formation of silver chloride. The action is rapid at a red heat. Silver sulphide is still more readily formed at all temperatures. Silver is dissolved by nitric acid and by boiling concentrated sulphuric acid.

Silver ores. The following are the more important: Native silver 97–99.8 p.c. Ag; the antimonide (*dyscrasite*), $\text{Ag}_2\text{Sb}-\text{Ag}_6\text{Sb}$; the telluride (*hessite*), Ag_2Te ; the sulphide (*argentite*), Ag_2S ; brittle silver ore (*stephanite*), $5\text{Ag}_2\text{S}, \text{Sb}_2\text{S}_3-68.3$ Ag; dark-red silver ore (*pyrarгыrite*), $3\text{Ag}_2\text{S}, \text{Sb}_2\text{S}_3-60$ Ag; light-red silver ore (*proustite*) $3\text{Ag}_2\text{S}, \text{As}_2\text{S}_3-65.4$ Ag; *polybasite* ($\text{Cu}_2\text{S}, \text{Ag}_2\text{S}$) $_9(\text{Sb}_2\text{S}_3, \text{As}_2\text{S}_3)-64-72$ Ag and 10.3 Cu; fahl ore (grey copper ore), either a complex antimonio-sulphide, arsenio-sulphide, or antimonio-arsenio-sulphide, containing variable quantities of silver, occasionally exceeding 30 p.c.; *stromeyerite* $\text{Cu}_2\text{S}, \text{Ag}_2\text{S}-53.1$ Ag; *horn silver* AgCl ; the iodide and bromide; and amalgams of varying composition.

Most ores of lead contain silver; indeed, this metal is of such constant occurrence with lead, that ores of the latter metal form one of the main sources of production of silver. Silver is also frequently present in ores of zinc and copper, and considerable quantities of the precious metal are annually derived from this source. It is also found occasionally in ores of iron, nickel, cobalt, and bismuth.

The curious spicular form of native silver, known as 'hair-silver,' is probably produced directly from silver sulphide, or silver selenide, either by reduction or simple dissociation (Kohlschütter and Eydmann, *Annalen*, 1912, 390, 340).

Extraction of silver from ores. The processes of silver extraction are very varied, owing chiefly to the diversity of the ores to be dealt

with. The methods may be classified under the following heads:—

1. Amalgamation.
2. Cyanide process.
3. Flotation.
4. Smelting, with subsequent separation of the silver from metallic lead or copper.

For the parting of silver from gold in bullion, *see* GOLD.

AMALGAMATION OF SILVER ORES.

It has long been known that silver cannot be extracted from its ores by amalgamation so readily as gold, on account of its lower density and its habit of being in combination. Silver ores yield only small percentages of their silver contents when crushed in stamp batteries and

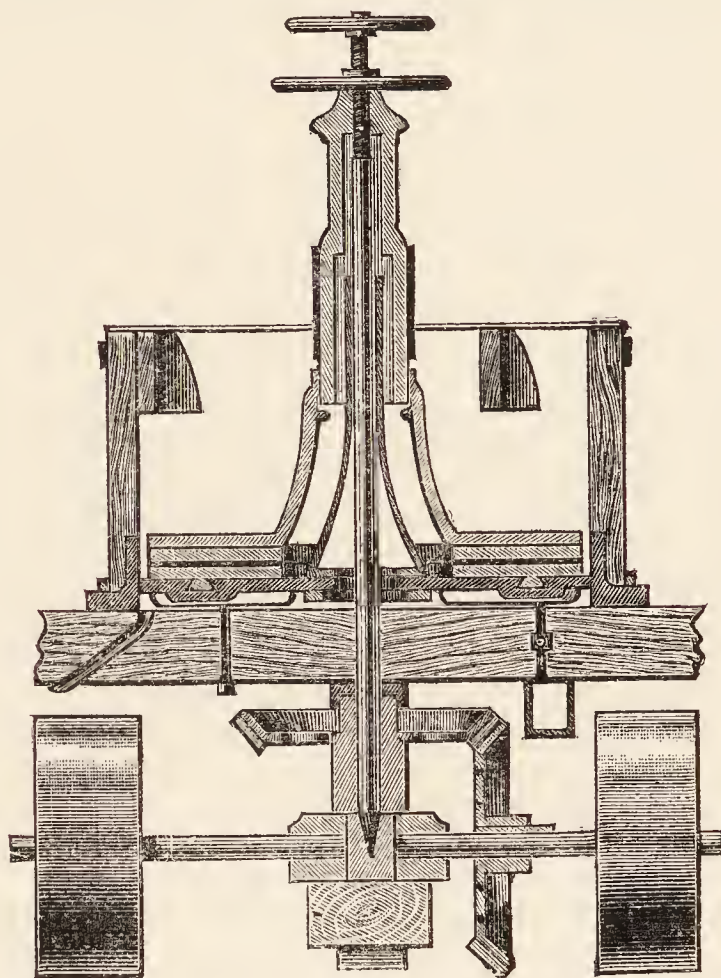


FIG. 1.

allowed to flow over amalgamated tables. Prolonged contact with mercury is required and some of the compounds of silver must be previously decomposed. Mercury reduces metallic silver from the chloride, bromide, iodide, and sulphide, and forms an amalgam with the reduced metal, but the action on the sulphide is very slow. Other compounds of silver, such as the complex sulphides containing arsenic, antimony, &c., resist the attack of mercury, and are converted into silver chloride before amalgamation by roasting the ore with common salt, or by the slow action of common salt and copper compounds at the ordinary summer temperature, as in the patio process.

The Patio, Cazo, Fondon, Krönke, Tina, and Freiberg barrel processes are all obsolete and need not be described.

In the *pan amalgamation process* crushed ore is ground to slimes in iron pans and then thoroughly mixed with mercury in the same vessels. An amalgamation pan is shown in Fig. 1. It consists of a flat-bottomed circular vessel about

5 ft. in diameter with a capacity of about $1\frac{1}{2}$ tons of ore to a charge. The bottom and lower part of the sides are of iron, and the upper part of the sides of wood. Through the centre of the bottom rises a hollow pillar within which is a revolving upright shaft to which are attached grinding plates or 'mullers.' These can be lowered so as to touch the bottom or raised some distance. The pan can be warmed by steam passed into the hollow bottom or jacket. The charge is run into the pan as a thick paste, and the mullers, which are already revolving, are then lowered and the pulp is ground between them and the bottom, detachable shoes and dies taking up the wear. After the pulp has been reduced to impalpable slime, the mullers are raised a little, mercury is added, and the charge is stirred for 2-4 hours longer. The consistency of the pulp is such that globules of mercury become dispersed through it without sinking to the bottom. Common salt and copper sulphate are added with the object of promoting amalgamation.

When the amalgamation is complete the speed of the mullers is reduced and the pulp is diluted by filling the pan with water. The mercury collects at the bottom of the pan and is drained off automatically into a sump, and the pulp is run off into the settling pan. This is similar to the amalgamating pan, but larger and provided with stirrers instead of grinding mullers. The pulp is further diluted and the lighter parts kept in suspension by stirring whilst the remainder of the mercury settles to the bottom and passes to the mercury sump, whence it is raised to the top of the building by a small ladder-bucket elevator. At intervals the silver is separated from the mercury. For this purpose the mercury is cleaned from sand, sulphides, &c., by grinding and stirring with water in a clean-up pan or barrel. The mercury is then strained through canvas, and the pasty amalgam recovered in the filter bags is retorted. The volatilised mercury is condensed under water and the residue left in the retort is melted and cast into bars.

The *Boss system* of pan amalgamation differs from that described above in being continuous in action. A number of pans and settlers are arranged in series, and the pulp from the stamp battery flows continuously through them, overflowing from each pan into the next successive one. The grinding is completed in the first pans, and the amalgamation is done in the later ones, the settlers recovering the amalgam.

Certain ores cannot be treated directly by the 'Washoe process' of pan amalgamation described above, but can be made to yield a high percentage of their silver by being roasted with common salt before being amalgamated ('Reese river process'). Silver sulphide is decomposed and silver chloride formed which is reduced to metallic silver chiefly by the iron of the pan and left in a readily amalgamable condition. The ores dealt with in this way are those containing the complex antimonial and arsenical silver sulphides and also 'dry' ores (*i.e.* those not especially suitable for smelting) containing silver sulphide mixed with sulphides of iron, copper, zinc, and lead. Ores containing large percentages of sulphides, especially galena, are usually smelting ores, and are

not suitable for treatment by roasting and amalgamation. In the Reese river process, the ores are first dried, usually in furnaces similar to those used in roasting, and are crushed dry in stamp batteries or ball or edge-runner mills. The preliminary drying before dry-crushing is required mainly to facilitate sieving.

For chloridising roasting the charge must contain some sulphide, unless MnO_2 is present in the ore. At Freiberg ores were formerly roasted with 20-30 p.c. of raw matte, but with some ores in the United States, as little as 6 p.c. of sulphide is found to be enough. An excessive quantity of sulphide gives rise to an undue consumption of salt and to avoid this, part of the sulphur is sometimes removed by roasting in air before the salt is added. The amount of salt required for roasting varies from 3 to 20 p.c., according to the ore. In the furnaces, sulphides are converted into oxides and sulphates, sulphurous and sulphuric anhydrides being given off. The sulphates and salt react, producing metallic chlorides and sodium sulphate. Chlorine and hydrochloric acid are also produced, and these act on metallic sulphides, oxides, sulphates, arsenates, antimonates, &c., yielding metallic chlorides as well as chlorides of sulphur, arsenic, and antimony.

After roasting the silver in the ore is mainly (up to 95 p.c.) in the form of chloride, which is mixed with chlorides, oxides, and sulphates of iron, copper, zinc, lead, nickel, &c. Some unaltered silver sulphide, arsenide, &c., as well as oxidised compounds of silver, are also present. The losses of silver in roasting are due to dusting and volatilisation, and vary with the form of furnace, the temperature, the current of air, the duration of the operation, and the nature of the ore. The losses of silver in a long-bedded calciner at Sonora were found by Clemes (Schnabel and Louis' Metallurgy, vol. i. 821) to be 11.6 p.c. at a dull-red heat, 13.7 p.c. at a red heat, and 15.9 p.c. at a cherry-red heat.

The furnaces used in roasting are reverberatories with hand or automatic stirring, rotating cylinders, and shaft furnaces. The automatic stirrers are usually attached to endless chains, half of which are outside the heated area. In rotating-cylinder furnaces the stirring is effected by the movement of the furnace, and the heat is supplied by flames passing through the cylinder. In some cylinder furnaces, *e.g.* Brückner and Hofman furnaces, the ore is charged in through manholes in the side of the cylinder, and the furnace is then closed and rotated until the roasting is completed, when the ore is discharged through the manholes. In White-Howell, Argall, and other furnaces, the cylinder is inclined and the ore passes through it continuously, entering at the end farthest from the fire. In shaft furnaces, such as the Stetefeldt, the ore falls in a shower through a rising current of hot air, the roasting of each particle being completed in a few seconds.

In general the ore is allowed to cool slowly, as the chloridising of the silver proceeds during cooling without increasing the loss of silver by volatilisation.

The pan amalgamation of roasted ore resembles that of unroasted ore already described. The silver chloride is reduced to

metal by the iron of the pan and mullers, before the addition of mercury.

The pan amalgamation process is nearly obsolete. No new mills have been erected for some time, and many of the old mills have been replaced by the cyanide or flotation processes.

THE CYANIDE PROCESS.

This process has been applied to the treatment of silver ores in many parts of the world during the last few years, especially in North America, and its use has been rapidly extending.

The ore is usually crushed very finely with cyanide solution. No preliminary roasting is required on most ores, the chloridising roasting at first practised in America having been given up. Stamp mills similar to those described under GOLD are in wide use for crushing. Sometimes fine battery screens are employed and the ore crushed fine in one operation. For example, at a mill at Guanajuato there were slotted screens equivalent to wire gauze with 45 meshes to the linear inch, the duty being only 2.7 tons per day per stamp (Caldecott, *J. Chem. Met. and Mng. Soc. of S. A.* 1908, 8, 203 and 266). More often coarse screens are used in the stamp battery, and the coarsely crushed pulp is passed to tube mills (*see GOLD*), where it is for the most part reduced to impalpable slime. The newer types of tube mills contain arrangements for rapid discharge, as, for example, by means of scoops which keep the level of the pulp below the discharge trunnion. The capacity is increased, but the ore is less finely ground. In a large and increasing number of cases, especially in America, ores are crushed in other machines, stamps being superseded. Among these machines are the Hardinge mill, the Marcy mill, the Marathon mill, Chile mills, and crushing rolls. The Hardinge mill (*Trans. A.I.M.E.* 1908, 39, 336) is a conical revolving mill containing steel balls or, for fine grinding, pebbles, by which the crushing is effected. It was first used instead of stamps at the Vipond mine, Ontario. The Marcy mill (*Mng. Mag.* 1916, 14, 232) is a short tube mill 8 ft. in diameter and 6 ft. long charged with large steel balls. In Chile mills or edge-runners (*Rose's Metallurgy of Gold*, 1915, 248) the ore is pulverised by heavy rollers running round on their tires in iron pans. At the Mexico mill, El Oro, 40 stamps crush 200 tons of ore per day through a 16-mesh screen, and six tube mills, each 4 ft. in diameter and 20 ft. long, deal with the product. After being finely ground in the tube mills, 90 p.c. of the pulp will pass through a 200-mesh screen (Caldecott, *l.c.*).

In crushing with cyanide no amalgamated copper plates are used, but with some ores, coarse native silver accumulates in the mortar boxes of the stamp mills and is from time to time collected by hand. The pulp from the stamps, or even from the fine grinders, is, in many cases, concentrated on Wilfley tables or other machines with the separation of material from which the silver would not be readily dissolved in cyanide, and this concentrate is shipped to a smelter together with any rich hand-picked ore that may come from the mine.

After concentration, if any, and fine grinding the larger particles ('sand') in the pulp are commonly separated from the fine particles

('slime') by settlement in water with the aid of such machines as Cone classifiers (*see GOLD*), the Dorr classifier, &c. The Dorr machine consists of a settling box in the form of an inclined trough open at the upper end, in which automatic rakes keep the slimes in suspension and remove the heavy material as fast as it settles. The liquid and slime overflow at the closed end. The sand is either returned to the tube mill ('all-sliming process') or treated by percolation with cyanide solution in large vats in which filter beds form false bottoms. The sand requires a lengthy treatment with cyanide, the solution being drained off and the charge aerated at intervals to facilitate the solution of the silver. Oxidising substances ('chemical aerators') are also added to assist the aeration.

The slime treatment consists in agitation with cyanide solutions and simultaneous aeration. Stirring gear in comparatively shallow tanks was formerly used for agitation, and the treatment continued for as long as 50 hours, the rate of dissolution of silver sulphide in cyanide solutions being very slow. When the solution is separated from the ore by decantation after mechanical agitation, the process is slow and incomplete, as the pulp cannot be allowed to settle completely before decantation owing to the difficulty of again setting the paddles in motion after the addition of water for washing. The result is that the residues remain somewhat rich both in silver and cyanide, and in order to reduce these losses, mechanical filters (filter presses and vacuum filters) were introduced to complete the work begun by decantation. These have proved so successful as to supersede washing by decantation for silver ores in America. Further reference is made to some of these filters below. Counter-current decantation is a later improvement, in which a current of cyanide solution rises upwards through settling ore and overflows at the top of the tank, to be introduced at the bottom of the next one, while the ore passes through the series of vats in the opposite direction. The system is tending to supersede the use of vacuum filters.

The Pachuca tank or Brown agitator making use of compressed air, is more advantageous than mechanical agitators. A sectional elevation of this agitator is shown in Fig. 2. The writer is indebted to the Cyanide Plant Supply Co., of London, E.C., for the illustration and also for the designs reproduced in Figs. 3 and 4. The Brown agitator was introduced in New Zealand in 1907, and afterwards adopted at the Pachuca mine, Mexico, whence its use spread widely. It is a steel cylindrical vat (*a*, Fig. 2) of, say, 45 ft. deep and 15 ft. in diameter. There is a pipe, *b*, in the central axis of about 1 in. diameter per foot of tank diameter, extending from near the bottom to near the top of the tank. At the bottom of the central tube compressed air is introduced from a pipe *c*, of about 1½ in. in diameter. The air pressure is at first as much as 50–100 lbs. per square inch, but afterwards it is regulated so as to be just enough to overcome the weight of the column of water at the point of introduction. The tank is filled with pulp with a relation of solid matter to water of say 1 : 1.5, and the air turned on, by means of the valve *g*, when part of the water in the central tube is displaced by air and

the centre column of material correspondingly reduced in weight. The result is that the central column is pressed up by the weight of the water in the surrounding tank and the pulp is effectively agitated and at the same time aerated. The bottom of the tank is a (reversed) cone, and there are no undisturbed portions of the pulp.

The Pachuca tank is suitable both for fine sands and slimes, and the power required is far

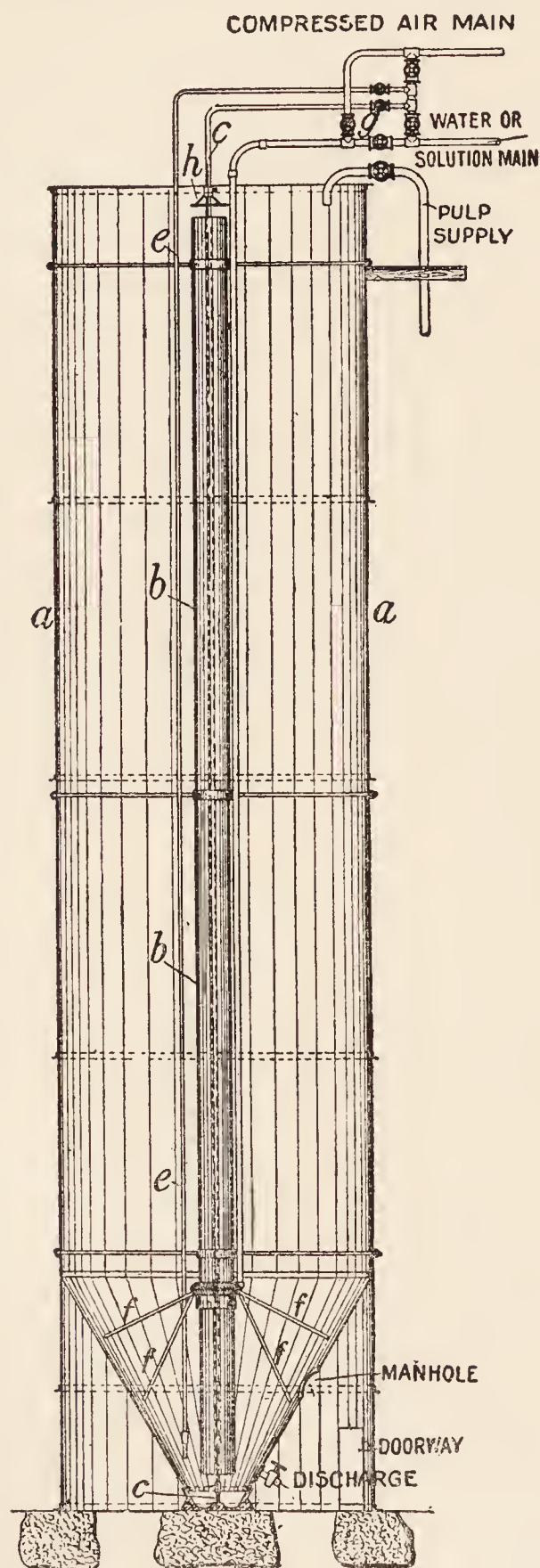


FIG. 2.

less than with mechanical stirring, being about $2\frac{1}{2}$ H.P. per 50 tons of slimed pulp, the charge in a 40-ft. by 10-ft. tank (James, Eng. and Ming. Jour. Jan. 1908, 17). Ordinary mill pulp is usually thickened by filtering off part of the cyanide solution before being charged into Pachuca tanks. The charge can be allowed to settle until the solid matter is packed down quite firmly before the air-jet is turned on. In that case water or solution is introduced through the

wash-ring *f*, in order to soften the material at the bottom of the cone. With the aid of this device the pulp is soon circulating perfectly, if it is very finely ground material, not containing heavy particles of sulphide, &c. These may cause difficulties, but they have been overcome and the efficiency of Pachuca tanks increased by the introduction by A. T. Grothe of a system of continuous work, the pulp overflowing from one tank to another until the dissolution of the silver is complete, the overflow from the last tank passing to a filter (Trans. A.I.M.E. 1911, 595). Other forms of tanks with air agitation are in use, such as the Trent, Parral, Hendryx, and Just agitators.

Slime from classifiers requires to be thickened, or de-watered, before it is fed into Pachuca tanks. The Dorr continuous thickener in wide use for this purpose consists of a shaft suspended vertically in the centre of a tank and carrying at its lower end radial arms, to which short pieces of angle iron are attached. When the shaft is rotated very slowly, the settled material is gradually moved to the discharge opening in the centre of the tank. The clear water overflows at the top of the tank.

The earliest of the rapid filters were filter presses in which the solution was forced through canvas by air under high pressure. These were first used with gold ores. The vacuum filters have been in use since 1903, and are very effective. In the Moore filter (Eng. & Ming. Jour. 1903, 76, 855; Trans. A.I.M.E. Sept. 1904) a vacuum filter frame is lowered into the pulp and kept immersed in it until a layer of slime of $\frac{3}{4}$ -1 in. thick is formed on the surface of the canvas. The filter frame is then hoisted out and the slime-cake is washed by clear water forced through it. When the cake is free from cyanide and silver it is detached by air blown into the inside of the filter. Among other successful vacuum filters are the Butters (Ming. and Sci. Press, June 22 & 29, 1907), and the Ridgway (Min. Ind. 1907, 16, 540). Fig. 3 is the plan and Fig. 4 the elevation of a vacuum filter plant (Cyanide Plant Supply Co.) of the fixed immersion type. Pressure filters, in which greater pressure is applied than is possible with vacuum filters, are also in wide use. The slime is pumped into narrow chambers between two filtering surfaces. In the Merrill press the slime-cakes, after being washed, are discharged by sluicing. Other forms are the Johnson, Burt, and Kelly presses. In all these filters lime gradually clogs the canvas, and after a time is removed by a bath of dilute hydrochloric acid.

The silver is precipitated from the clear solutions either by zinc-dust or zinc shavings. Zinc-dust is mixed with the solution in tanks and separated by filter pressing, but zinc shavings are contained in boxes through which the solution is allowed to flow. The solutions are less dilute in cyanide than those used for gold ores, and contain large quantities of silver, and owing to these facts coarse zinc shavings are used, not coated with lead. The zinc-silver couple, soon formed by precipitation of the silver, gives a high precipitating efficiency to the zinc and enables the lead-zinc couple to be dispensed with.

In recovering the silver from the zinc boxes, simple screening of the precipitate separates the

zinc and gives a product containing 50–70 p.c. of silver, which is briquetted by air pressure, partly dried, and smelted with 2 p.c. of nitre without any treatment with acid or by roasting. Large (No. 300) graphite pots or steel pots are

used. The silver thus produced is somewhat impure and is sometimes refined by passing air through the molten bullion, as proposed by Rose (*see Min. Ind.* 1910, 320). Aluminium powder was introduced as a precipitant instead

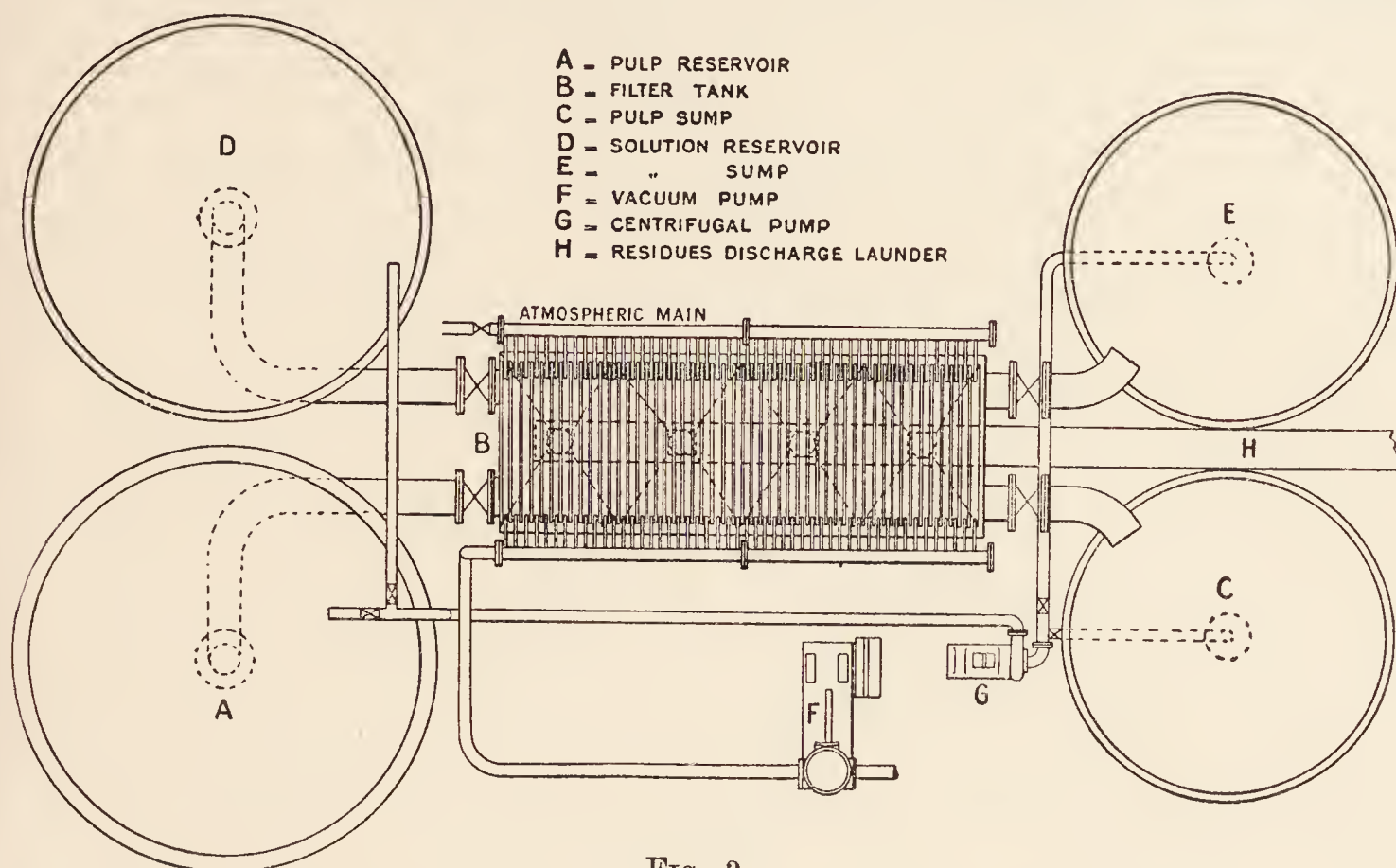


FIG. 3.

of zinc at Deloro and Nipissing, Ontario (*Eng. and Mng. J.* May 10, 1913, 935), but the price of aluminium dust became excessive during the war, and sodium sulphide was substituted in 1916 (*Bull. Can. Mng. Inst.* Nov. 1916). The precipitated sulphide is reduced by caustic soda and aluminium ingots.

The cyanide consumption on Mexican silver ores varies from 1 to 4 lbs. per ton, and 70–90 p.c. of the silver is recovered. Although power in Mexico is cheap (30s. per H.P. per month for transmitted electric power) and unskilled peon labour is only 1s. 6d. per day, the cost of treatment, according to Caldecott, was heavy in 1908,

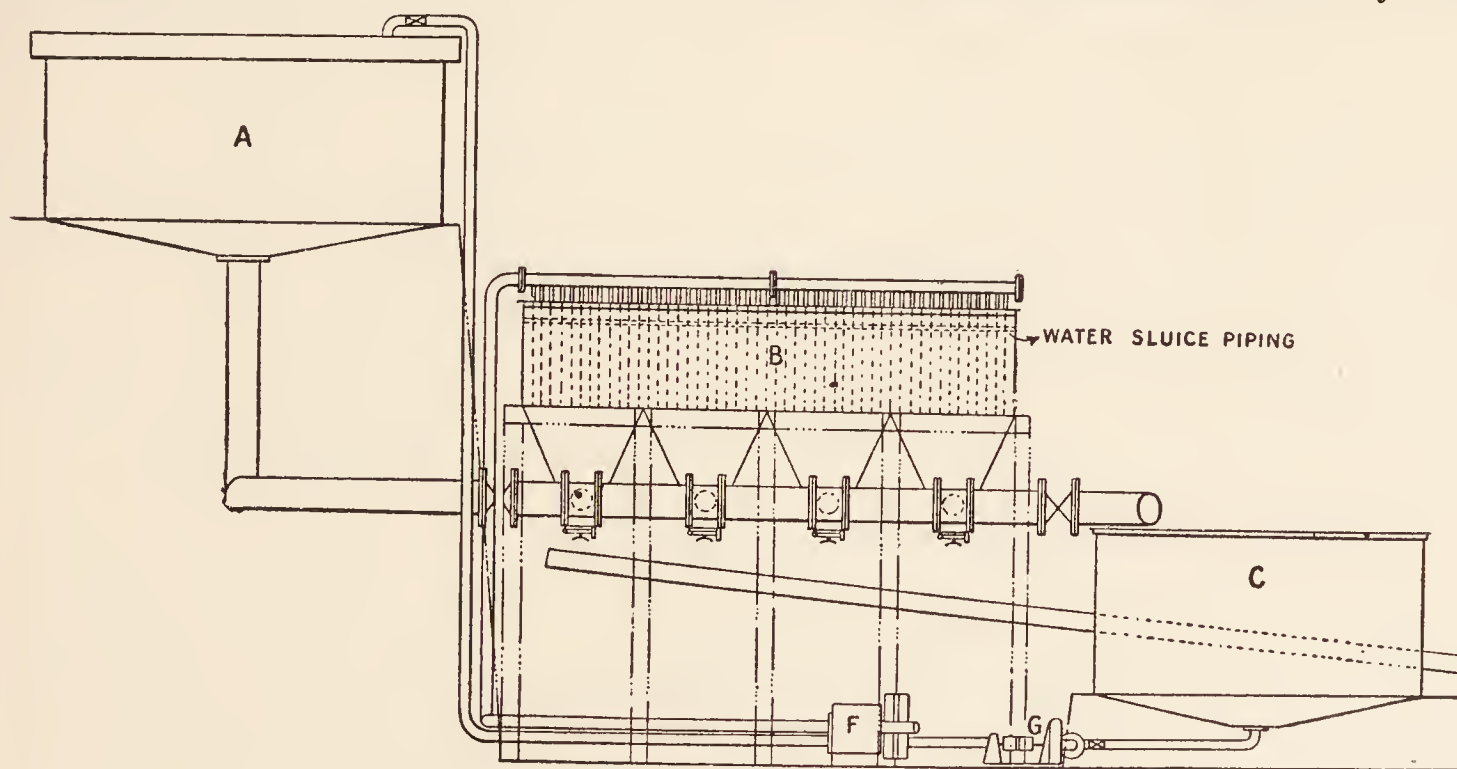


FIG. 4.

varying from 8s. to 12s. per ton. This is due to the high consumption of cyanide and the large amount of power required for the fine grinding in vogue. The cost is now much lower in many United States mills. For example, at the Nevada Packard, Nevada, the cost in 1916 was \$1.23 with a recovery of 95 p.c. (*Mng. Sci. Press.* 1916, 112, 377).

The strength of the cyanide solutions has a considerable range. The solution used in the stamp mills contains 0.1 p.c. of cyanide upwards. At the San Rafael mine, Mexico, the mill solution contained 0.25 p.c. in 1909 (*Girault, Proc. Inst. of Metals*, 1910, 4, 288). The solutions for slime treatment usually contain about 0.3 p.c. of cyanide. In the treatment of sands, solutions

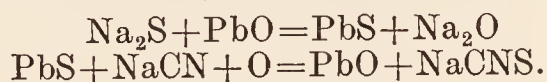
with 0.5 p.c. or even more cyanide are not uncommon.

It is usual to add to the slime pulp from 4 to 12 ozs. of lead acetate or litharge per ton of dry slimes. This is intended to remove the deleterious soluble sulphides from the solution, but doubts have been expressed as to its usefulness, on the grounds that the quantity would be insufficient without aeration, and efficient aeration should be enough without lead salts.

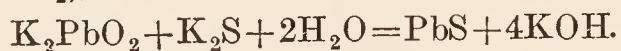
The chemistry of the process presents some features which are different from those met with in the treatment of gold ores. The ores treated in Mexico usually consist of hard flinty quartz containing little base metal mineral (Caldecott). The greater part of the silver is present as argentite, Ag_2S , with a little arsenic and antimony as proustite, pyrargyrite, and stephanite. Native silver and the haloid compounds sometimes occur, and these dissolve readily. Argentiferous tetrahedrite, galena, or blende when present prevent the use of cyanide unless they can be removed as concentrates.

Silver sulphide is dissolved according to the equation: $\text{Ag}_2\text{S} + 4\text{NaCN} = 2\text{NaAg}(\text{CN})_2 + \text{Na}_2\text{S}$. This reaction is reversible, and in dilute solutions about 100 molecules of NaCN must be present to 1 molecule of Na_2S to prevent reprecipitation of Ag_2S . By aeration, however, the alkaline sulphide is oxidised to thiosulphate and caustic alkali, and subsequently to sulphate. The following reaction also occurs, but far more slowly: $\text{Na}_2\text{S} + \text{NaCN} + \text{O} = \text{NaCNS} + \text{Na}_2\text{O}$.

As an aid to aeration in the removal of Na_2S , lead salts (acetate or even litharge) or mercury salts, such as HgCl_2 , are added, with the result that lead or mercury sulphide is precipitated and redissolved by cyanide in the presence of air with the formation of alkaline sulphocyanide and the regeneration of litharge, thus:—



This accounts for the great effect of a few ounces of lead salts per ton of ore in which some hundreds of ounces of silver sulphide may be present. The solution is strongly alkaline, *e.g.* in Mexico 20 or 30 lbs. of lime per ton of ore is used, with the object of increasing the solubility of silver compounds. Part of the lime dissolves in the cyanide solutions, but the bulk of it remains in the form of milk of lime. The alkali converts litharge or lead acetate into an alkaline plumbite (K_2PbO_2), and this reacts as follows:—



It was found by Holt (Ming. & Sci. Press, 98, 546; 99, 159) that if the silver is present in the form of proustite (Ag_3AsS_3), pyrargyrite (Ag_3SbS_3), or tetrahedrite (fahlore), the presence of lead salts in addition to lime seems to retard rather than assist dissolution. These minerals yield their silver to cyanide satisfactorily only if subjected to a chloridising roast. Mangiferous silver ores are also generally refractory to cyanide. A chloridising or reducing roast followed by cyaniding is sometimes efficacious (J. Chem. Met. Mng. Soc. of S. A. 1916, 17, 9).

A combination of amalgamation and cyaniding applied to certain ores in Mexico is described by Brodie (Mex. Ming. J. 1911, 12, 21; J. Inst. of Metals, 1911, 5, 297). The ores contain

galena, blende, and pyrite, and various amounts of silver, down to 4 ozs. per ton, in the form of native silver, argentite and arsenical silver. The high-grade ore is crushed direct by stamps, and some native silver remains in the mortar and is collected from time to time. The pulp is then amalgamated in 4-ft. pans, the charge consisting of 1000 lbs. of ore, 15–17 lbs. of mercury, 45 lbs. of sodium cyanide, 4 ozs. of lead acetate, $3\frac{1}{2}$ lbs. lime and stock solution to make a 1 : 1 pulp.

Grinding without mercury is carried on for 6 hours, followed by 10 hours' mixing with mercury. The charge is then transferred to a settler where it is leached and agitated mechanically and by compressed air for 12 hours. After this it is washed free from mercury, thickened, and treated in Pachuca tanks.

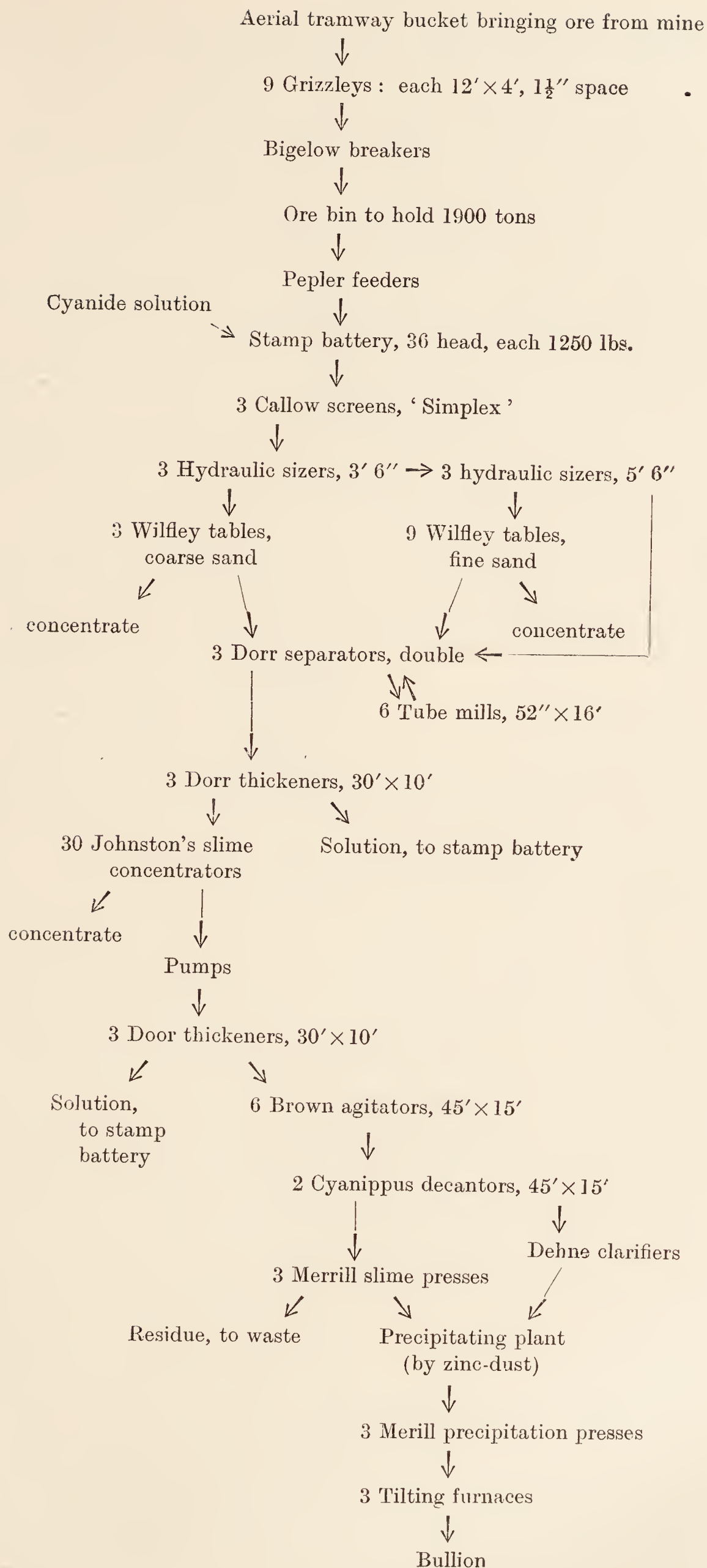
The low grade ore is concentrated in the ratio of 50 : 1, and the concentrates are separated into rich and poor material. The rich concentrates are amalgamated as described above but for 2–5 days, and treatment in the settler lasts for 6 days, with decantation each day. Then the product goes to the Pachuca tanks. The poor material is leached in percolating tanks with cyanide (50 lbs. per ton of concentrates), lime and lead acetate. The charge is treated by percolation for 12 hours and then the liquid is drained off and the charge aerated for 12 hours. This alternate treatment is continued for two months or until 95 p.c. of the silver has been extracted.

The system of treatment of silver ores by cyanide now adopted is complicated, as is illustrated by the following abridged 'flow sheet,' which was recently designed (and kindly lent for reproduction) by Mr. Alfred James for a mill to be erected by a large mining company in Mexico. The abridged sheet is simplified by omission of the sampling arrangements and certain other features which form an essential part of the design. The flow sheet is shown opposite.

Regeneration of cyanide has been introduced recently. The cyanide solutions after passing through the ore are acidified with SO_2 , by which the silver is precipitated, and the cyanide converted into HCN . The filtered solution is exposed in films or sprays to a current of air under reduced pressure. The hydrogen cyanide is taken up by the air and re-absorbed in alkaline solutions for further use (Eng. and Min. J. Press, Jan. 19, 1924, p. 107).

Among other lixiviation processes for the treatment of silver ores the following may be mentioned:—

The *Ziervogel* process is applicable to argentiferous copper mattes, free from As, Sb, Bi, and Pb. These mattes are formed in smelting and consist chiefly of sulphides of copper and iron. They are now usually smelted for copper, from which the silver is separated by electrolysis. In the Ziervogel process the matte is roasted in an oxidising atmosphere at a gradually increasing temperature with the formation of sulphates. Sulphate of iron is formed first together with some oxides of iron and copper. At a temperature of about 700° , however, the iron sulphate is decomposed, sulphur dioxide and oxygen are evolved and copper sulphate is produced. Then as the temperature rises CuSO_4 is converted into



$2\text{CuO}\cdot\text{SO}_3$ at 740° , and into CuO at 840° – 850° (Friedrich, *Metallurgie*, 1910, 7, 323). At the same time silver sulphate is produced. Finally at a bright red heat (1085° , according to Friedrich) silver sulphate is split up and metallic silver remains with the oxides of iron and copper. The action is carefully watched and the operation stopped when the copper sulphate has been almost all decomposed, and the silver sulphate is at its maximum. The roasted matte is then extracted with hot water, and the silver precipitated by means of metallic copper. The process requires skill and care, and the losses of silver are by no means insignificant.

In another group of processes the silver in sulphide ores is roasted with salt with the production of silver chloride, which is dissolved by a hot solution of common salt (*Augustin process*), by sodium thiosulphate (*von Paterna process*), or by calcium thiosulphate (*Kiss process*). In the *Russell process* a solution of sodium-copper thiosulphate ('extra-solution') is used after the ordinary thiosulphate has been drawn off. In this way some metallic silver and undecomposed silver sulphide is extracted as well as the silver chloride. Precipitation is effected by metallic copper in the Augustin process, and by a soluble sulphide when a thiosulphate is used as the solvent for silver. These processes are now obsolete, being generally less advantageous than cyaniding.

FLOTATION.

When oil is mixed with ore and water, it tends to rise to the surface, carrying with it sulphides and certain other compounds of the heavy metals, and leaving the earthy particles to settle to the bottom. Air or other bubbles when formed into a froth also adhere selectively to heavy sulphides and tend to make them float. The addition of a little oil facilitates froth-flotation. These methods of concentration by flotation have been applied to silver ores to some extent, and appear likely to supersede the cyanide process in many cases. The concentrates are usually smelted, but in outlying districts far from a smelter they are sometimes treated by cyanide. The oil is removed by roasting or in other ways, the concentrates are ground finer if necessary and are agitated with cyanide. In some cases it has been profitable to treat tailings dumps from the cyanide process by means of flotation. For details of the various modifications and machinery employed, see COPPER. See also T. J. Hoover's *Concentrating Ores by Flotation*, 2nd ed., London, 1914; *The Flotation Process*, by T. A. Rickard, San Francisco, 1916; *A Contribution to the Study of Flotation*, H. L. Sulman, *Trans. I.M.M.* 1920, 29, 44.

SMELTING SILVER ORES.

Argentiferous lead and copper ores are smelted for lead and copper respectively, the silver being concentrated in the resulting pigs of metal or in mattes, speiss, or other intermediate products. In making up the charges for the blast furnaces in lead smelting, poor sulphide ores are first roasted and all silver ores, even if they contain no lead, may be mixed with the lead ore and their silver extracted. In each

case consideration is paid to the composition of the silver ore and to the possibility of treating it more profitably in other ways. The lead usually amounts to 10 or 12 p.c. of the charge, and the coke to from 7.5 to 16 p.c. Blast furnaces of moderate size are used and argentiferous lead, some matte, and a fusible slag consisting chiefly of silicates of lime and iron with various impurities are produced. For the details of smelting, see LEAD and COPPER.

The pig lead or 'base bullion' contains varying quantities of silver up to about 2 p.c. It is not usual to allow this proportion to be exceeded on account of loss in the slag. The distribution of silver in the lead is irregular and it is difficult to obtain trustworthy samples for assay. The most satisfactory method is to melt the lead and to dip out a small part as a sample.

The *desilverisation of lead* is effected by the Pattinson process, now almost obsolete, by the Rozan process, or by Parke's process, followed in each case by cupellation. In the Pattinson process a charge of 10 or 15 tons of molten lead contained in an iron pan is allowed to cool, and the crystals of nearly pure lead first formed are separated from the mother liquor, which contains practically all the silver. In the original Pattinson process the crystals were removed by perforated ladles and the operation continued until the enriched lead contained about 1 p.c. of silver. The limit of richness would be reached when the lead contained 2.5 p.c. of silver, the composition of the eutectic alloy. In a later modification of the process the charge is kept stirred by revolving paddles or by jets of steam (Rozan process) and the mother liquor drawn off by tapping, after about two-thirds of the lead has been converted into crystals. The operation is repeated until the rich lead contains about 2 p.c. of silver, and the poor lead from 0.001 to 0.003 p.c.

Parke's process depends on the fact that if molten zinc is stirred into a bath of argentiferous lead, which is afterwards allowed to cool somewhat, the zinc extracts the silver from the lead, and rises to the top forming a crust, which contains the silver and any gold or copper that may be present. The total amount of zinc added is usually about $1\frac{1}{2}$ or 2 p.c. of the weight of the lead, but it is not all added at once. Two or three successive additions are made, and the crusts removed by perforated ladles as soon as they begin to form. The first crust contains almost all the gold and copper. Only about 0.0005 p.c. of silver is finally left in the lead, which also retains 0.6 p.c. of zinc.

The zinc crusts contain much lead which is in part separated by liquation, the crust being heated to the melting-point of lead, when some of the lead flows away. After liquation the rich scums are usually treated by retorting, the zinc being distilled and recovered for further use. Faber du Four tilting furnaces (Fig. 5), each containing a single large pear-shaped graphite retort, are in wide use. These furnaces take a charge of 8–10 cwts. of rich scums. After distillation the residue consists chiefly of lead and silver, containing from 5 to 10 p.c. of the latter. It is treated by cupellation.

Another method of treating the rich scums is to oxidise the zinc with steam and dissolve it

in sulphuric acid. This method can be used only if there is a ready market for the zinc sulphate. In the Schnabel process the zinc oxide is dissolved out by ammonium carbonate. For further details concerning the desilverisation of lead, see LEAD.

The electrolytic method used in the desilverisation of copper has already been described under COPPER.

Cupellation consists in melting argentiferous lead in a reverberatory furnace and oxidising it by means of a blast of air which is directed upon its surface. The litharge flows to the edge of the molten bath of metal, carrying with it the oxides of other base metals, and is drawn off through narrow channels in the hearth. When all the lead has been oxidised the silver remains in the furnace in a partially refined state. The hearth of the furnace consists of marl, boneash, Portland cement and crushed firebrick, or magnesia, materials which resist the corrosive action of molten litharge. The temperature is

kept above the melting-point of litharge, which is from 825° to 900° , as pasty litharge is likely to carry away considerable quantities of entangled silver.

The litharge formed at the beginning of cupellation contains the greater part of the readily oxidisable impurities such as iron, zinc, and tin. Arsenic and antimony are oxidised more slowly, and copper, bismuth, and tellurium are retained by the metal bath until most of the lead has been removed. Molten litharge absorbs oxygen from the air, and gives it up again to copper, bismuth, &c., which are in great part oxidised in that way. Silver is lost by volatilisation and also by being carried away in the litharge, which, according to Kohlmeyer, dissolves from 3 to 6 p.c. of silver, probably as oxide in the first place. The total loss of silver is usually not more than 0.5 p.c. Cupelled silver may be 998 fine, containing only 2 parts of impurities per 1000, but is often impure, requiring to be cupelled again with fresh lead.

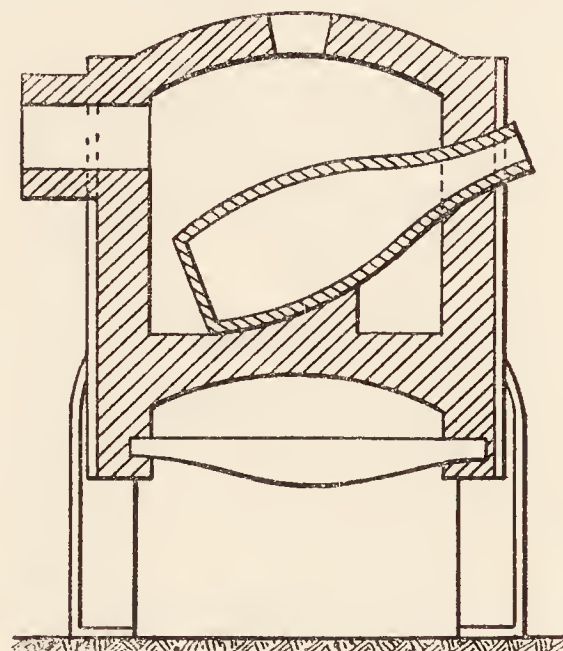
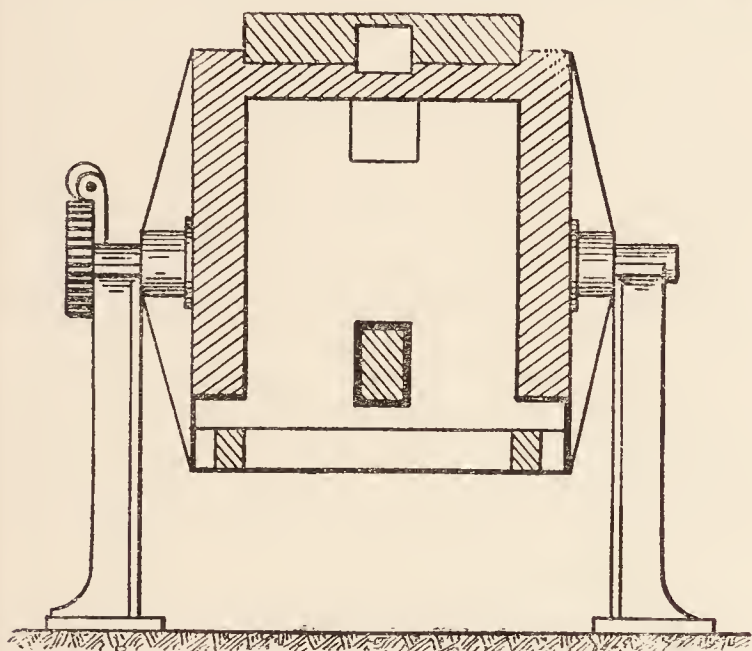


FIG. 5.

The separation of litharge from the metal-bath is due to its lower density and lower surface tension. Anything that lowers the surface tension of the metal-bath increases the loss of silver (Smith, Trans. I.M.M. 1908, 17, 463).

There are two types of furnace, the German and the English cupellation furnaces. The German furnace takes a charge of from 5 to 30 tons of argentiferous lead. It has a fixed hearth forming part of the furnace and a movable top or hood which is lifted off by a crane, when the work is at an end, to facilitate cooling, the removal of the silver, &c. The charge is melted very slowly so as to eliminate certain mechanically mixed impurities, especially sulphides and copper, which form a dark scum (*Abzug*) on the surface of the molten metal, and are raked off before the blast is turned on. Then *Abstrich*, consisting chiefly of arseniates and antimonates, is formed and raked off, after which pure litharge (*glätte*) is formed and allowed to flow away. The litharge is often sold as such, without further treatment. Towards the end of the operation the litharge becomes more and more contaminated with copper, bismuth, &c. The final result, in one method of working, is an impure silver (*Blicksilver*) containing 5–10 p.c. of impurities. The silver is allowed to solidify and

the cake is cooled with water, broken into pieces while still hot, and refined by a second cupellation (*Feinbrennen*) with fresh lead in a special furnace or by treatment in pots. The fine silver is cast into bars.

The English cupellation furnace has a fixed hood, but the hearth or test is removable from the furnace. It is much smaller than the German furnace, containing from half a ton to five tons of work-lead. It is used for richer silver-lead alloys than the German furnace. The litharge produced usually contains too much silver for it to be sold without further treatment. The silver-lead is usually enriched until it contains 50–70 p.c. of silver, when it is ladled out into moulds and a fresh charge added to the furnace. The test eventually wears thin, when it is withdrawn and another test substituted. Rich silver-lead is cupelled to pure silver in a separate furnace at a higher temperature than before, and is then ladled out into moulds.

In Fig. 6 an American type of English cupellation furnace is shown, described by Hofman (*Metallurgy of Lead*, 5th ed. 519). The plan is on the section *xx* in the elevation. Here *a* is the fireplace, *b* the test, and *c* the flue. The space underneath the test is hollow. In this

furnace the test is 4 ft. 4 ins. by 3 ft. 6 ins., and the old oval shape has been modified. For further details of cupellation, *see* LEAD.

Refining.—Silver bullion produced by the methods already described usually contains gold as well as impurities such as copper, iron, lead, zinc, &c. For the methods of parting it from gold, *see* GOLD. In these processes the base metals are also separated. Doré silver containing only a few parts of gold per 1000 is either treated alone or melted with crude gold bullion with the formation of a parting alloy.

The anode mud formed in the treatment of argentiferous copper by electrolysis (*see* COPPER) may contain a high percentage of silver. For example, a sample of anode slimes from converter copper at Anaconda was found by Keller (*J. Amer. Chem. Soc.* 1897, 19, 10; *Min. Indus.* 1898, 239) to contain 55.15 p.c. of silver and 0.20 p.c. of gold, together with 13.82 p.c. of copper, 10.68 p.c. SO_4 , and 8.35 p.c. of Pb, Bi, Sb, As, Te, Se, and Fe. Such material was formerly treated by boiling with sulphuric acid

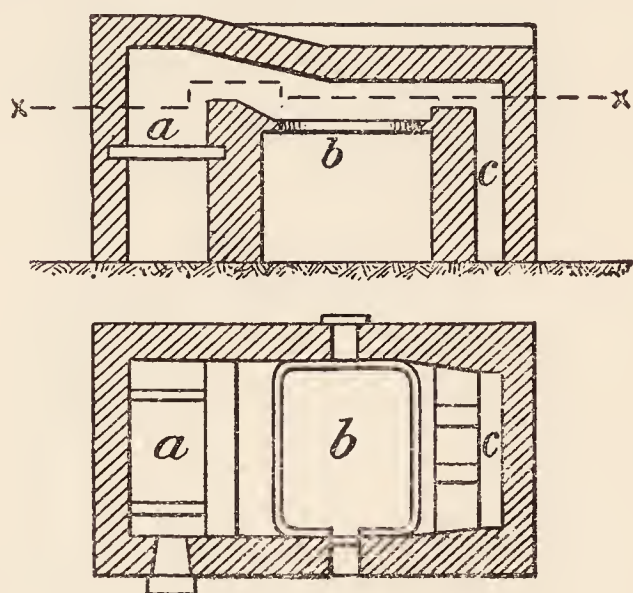


FIG. 6.

and precipitating the silver by copper. Various modifications of this process have been introduced such as the Cabell-Whitehead process of boiling with silver sulphate and dilute sulphuric acid, by which the copper was obtained in solution and the silver in the residue. Lead, arsenic, &c., may be removed by melting in a reverberatory furnace, or, if present in small quantities only, by treatment in crucibles. The Moebius process of electrolysis is described under GOLD.

Silver obtained by amalgamation, by the lixiviation processes, or in the form of 'Blicksilver' by cupellation is often refined in crucibles. In Rössler's process (Schnabel and Louis' *Metalurgy*, vol. i. 729) silver sulphate is added to the metal to eliminate lead, bismuth, and more oxidisable metals. The silver is melted in plumbago crucibles and covered with a layer of sand. The silver sulphate is then added and stirred in with an iron rod. It is decomposed (at 1085° , according to Friedrich) into silver, sulphur dioxide, and oxygen, and the base metals are oxidised by the latter. At Lautenthal three or four successive additions of silver sulphate are made in treating 'Blicksilver' which is 950–980 fine, the total amount of silver sulphate added being from $1\frac{1}{2}$ times to twice the weight

of the impurities. The slag consists of silicates of iron, lead, bismuth, &c., and contains 1.88 p.c. of silver according to an analysis by Hampe.

Another method of refining such silver is to pass air through the molten metal contained in pots and covered by a layer of sand and borax (Rose, *Trans. I.M.M.* 1905, 14, 377).

Cement silver which contains silver chloride is melted with caustic potash or soda. Thus at Schmöllnitz (Schnabel and Louis, *l.c.*) 246 lbs. of cement silver are melted in a plumbago crucible with $1-5\frac{1}{2}$ lbs. of caustic potash in order to decompose the silver chloride and 5–20 ozs. of saltpetre for the oxidation of antimony, &c. The process lasts about 6 hours.

Uses of silver.—Silver is mainly used in the form of its alloys with copper for conversion into coin, plate, and jewellery. The alloys used in coinage contain from 400–945 parts of silver per 1000, the most usual standards being 500, 900, and 916.6 (*see* Report by Imperial Mineral Resources Bureau on Silver, 1913–1919, p. 13, London, 1923). For details of coinage, *see* GOLD. Silver wares are of many different standards (*see* Rose's 'Precious Metals,' 245). The British standard is 925 fine for wares.

Silver plate often contains 0.5 p.c. of cadmium to facilitate the production of sound malleable castings. The ingots of silver are rolled out into sheets, which are pickled and slit into strips for the production of wire, or stamped out and the pieces shaped by striking between dies. 'Stainless silver,' an alloy of silver 92.5 p.c. with copper and some antimony is now also used for wares. It resists the blackening action of sulphur compounds in the air of towns. Silver-plating is carried out in cyanide baths containing about 3 ozs. of potassium cyanide and 1 oz. of silver per gallon of water.

Production of silver.—The annual production of silver rose almost continuously from 1830 to 1912, but decreased in the years 1913–1921. In 1830 the world's production was about 460,000 kilogs., in 1880 2,500,000 kilogs., in 1900 5,600,000 kilogs., and in 1912 233,060,753 ozs. or 7,249,000 kilogs. The production depends largely on that of lead and copper by smelting, in which silver is a by-product. According to the Imperial Mineral Resources Bureau, the annual production of silver during the period 1919–1921 was as follows:—

	1919	1921	1920
Silver, fine oz. } 177,000,000	177,800,000	172,000,000	

The largest amount of silver is produced by Mexico, followed by the United States and Canada. These three countries between them account for about 75 p.c. of the world's product. The price of silver is quoted in London in pence per standard oz., 925 fine, and in the United States in cents per fine ounce. It was about 60 pence per standard ounce from 1830 to 1873, but afterwards it fell almost continuously with some fluctuations until 1902, when it was 24 pence. The price in Feb. 1920, had risen to $89\frac{1}{2}$ pence per standard ounce, and was about 35 pence in Sept. 1924.

Alloys of Silver. The *silver-copper* alloys are, commercially, by far the most important of these. The addition of a few per cent. of copper to silver lowers its melting-point, prevents it from

effervescing on solidification, enables sound castings to be made, and makes it harder without sensibly impairing its malleability or altering its colour. The superiority of such alloys over pure silver, as well as their lower cost, led to their use in coinage and for ornaments in very early times. For the melting-points of the alloys, see Heycock and Neville (Phil. Trans. 1897, 189 A, 25). Levoll's alloy, containing 71.89 p.c. of silver, is the alloy of lowest melting-point (eutectic alloy), solidifying at 778°. This alloy is uniform in composition, but in the others segregation takes place on solidification, those containing more than 71.89 p.c. of silver, becoming richer in silver in the interior than on the outside, and those with less than 71.89 p.c. of silver changing in the reverse direction. The difference in composition, however, between the inside and the outside of an ingot never exceeds a few parts per thousand. For the specific gravity of the alloys, see Karmarsch (Dingl. poly. J. 1877, 226, 335). The density of British silver coin and plate (925 fine) is 10.37, and that of the 900 standard is 10.31. For the properties of standard or sterling silver, with notes on its manufacture, see E. A. Smith and H. Turner, J. Inst. Metals (2), 1919, xxii. 149. Various standards, down to 250 fine are in use for coinage. The silver-copper alloys blacken when heated in air, but the black oxide of copper is removed and a frosted surface of pure silver produced by treatment with dilute sulphuric acid, to which dichromate of soda is added to prevent the formation of red stains.

Silver and lead mix together in all proportions when molten, but on solidification they separate completely and the alloys undergo segregation, so that they are not uniform in composition. The valuation of argentiferous lead produced in smelting is therefore difficult. The eutectic alloy contains 2.5 p.c. of silver and solidifies at 304°. This freezing-point is observable even in an alloy containing over 99 p.c. of silver (Petrenko, Zeitsch. anorg. Chem. 1907, 53, 200). In alloys containing less than 2.5 p.c. of silver, crystals of nearly pure lead separate out between 327° and 304°. The Pattinson process of desilverisation of lead is based on these properties.

Silver-bismuth alloys are similar to the silver-lead alloys. The eutectic contains 2.5 p.c. of silver and solidifies at 262°. It persists almost to the pure silver end of the series, making all the alloys brittle, particularly if copper is present also. In the latter case annealing is useless, so that a trace of bismuth makes standard silver unfit for coinage.

Silver-mercury alloys. See AMALGAMS.

Silver-gold alloys. See GOLD.

Silver-zinc alloys are readily formed, zinc removing silver from molten silver-lead alloys. It is probable that in this case the compound Ag_2Zn_3 is formed, which melts at about 430°, and rises to the top of the lead-bath forming a crust in which some lead is entangled. The zinc can be removed from the alloy by distillation or treatment with acid.

Alloys of silver with tin, platinum, aluminium, thallium, cadmium, manganese, arsenic, glucinum, tellurium, and nickel have also been studied.

Bibliography.—Detailed information on the

metallurgy of silver may be found in Percy's Silver and Gold, 1880, H. F. Collins' Metallurgy of Lead and Silver, 1900, Schnabel and Louis' Handbook of Metallurgy, 1907, Rose's Precious Metals, 1909; in the transactions of various societies such as the Institution of Mining and Metallurgy, London, the American Institution of Mining Engineers, and the Chemical, Metallurgical, and Mining Society of South Africa.

T. K. R.

Colloidal silver was first obtained by Carey Lea (Amer. J. Sci. 1889, 37, 476; *ibid.* 38, 47, 129; *ibid.* 1894, 48, 343; Phil. Mag. 1891, 31, 238, 320, 497; 32, 337) by the reduction of silver salts with the metallic salts of organic and inorganic acids. Dextrin or tannin may also be used as reducing agents. Colloidal silver is prepared by adding to 500 c.c. of a 10 p.c. silver nitrate solution, a mixture of 280 grms. of crystallised sodium citrate dissolved in 500 c.c. of water and 500 c.c. of a 30 p.c. solution of crystallised ferrous sulphate with constant stirring. The precipitate is washed by decantation with dilute sodium citrate solution, dissolved in water and reprecipitated by the addition of absolute alcohol. As thus prepared it is a pale lilac, blue or green-coloured mass forming a deep-red aqueous solution. It may also be prepared by adding a strong solution of formaldehyde to silver oxide in water at 35°.

Colloidal silver may be prepared by passing an electric current between silver poles under water. With a small current brown solutions of low conductivity are obtained, whereas with stronger currents, the particles of silver increase in size and the solutions become greenish or bright green, and possess a greater conductivity. The conductivity of colloidal silver solutions, which is greater than that of water, is supposed to be due to the presence of silver oxide (Rebière, Compt. rend. 1909, 148, 354). The addition of an electrolyte also converts the brown into a green solution (see also Woudstra, Zeitsch. physikal. Chem. 1908, 61, 607; Lottermoser, *ibid.* 62, 284).

An electrical method of preparing aqueous colloidal solutions of silver has been described by Morris-Airey and Long, which involves the use of a high-frequency alternating arc, a suitable generator being provided by the Poulsen arc. Such solutions of colloidal silver are very stable and can be concentrated by boiling (Long, Kolloid Zeitsch. 1914, 14, 136; Rebière, Bull. Sci. Pharmacol. 1917, 24, 193).

Solutions of colloidal silver are also said to be obtained by heating silver with distilled water for a long time (Traube-Mengarini and Scala, Atti R. Accad. Lincei, 1909, [v.] 18, 542).

Colloidal silver may also be obtained by heating silver nitrate with an alkaline solution of proto- or lys-albinate (Paal, Ber. 1902, 35, 2206), or with formaldehyde and sodium silicate, or with wool-fat (Amberger, Zeitsch. Chem. Ind. Kolloide, 1912, 11, 97; Küspert, *ibid.* 1902, 35, 2815, 4066, 4070), or with acetaldehyde and gelatin solution (Castoro, Gazz. chim. ital. 1907, 37, i. 391). In the last case the solutions have the colour of bromine and may be kept for years without changing their colour or properties.

For the protective influence of starch, v.

Gutbier and Weingärtner, Koll. Chem. Beihefte, 1913, 5, 211.

According to a U.S. Pat. (701606, 1902) a colloidal silver, distinguished by its property of retaining its solubility in dilute alkalis after having been precipitated from aqueous solutions by acids, is obtained by the action of silver chloride on an alkaline solution of the products of decomposition of albumins by warm dilute alkalis (J. Soc. Chem. Ind. 1902, 916).

Colloidal silver is chemically active towards a number of substances. It reduces mercuric chloride, ferric chloride, and an acid solution of potassium permanganate. A solution of iodine in potassium iodide converts it into silver iodide. It reduces silver nitrate to nitrite, reacts with hydrogen cyanide and the alkali cyanides and forms salts with the halogens.

For other methods of preparing colloidal silver, see Schneider (Ber. 1891, 24, 3370; 1892, 25, 1164, 1281, 1440); Barus and Schneider (Zeitsch. physikal. Chem. 1891, 8, 278; Wied. Ann. 1893, 48, 357); Oberbeck (*ibid.* 745); Blake (Amer. J. Sci. 1903, 16, 282); Lottermoser and Meyer (J. pr. Chem. 1897, 56, 241; *ibid.* 1898, 57, 540); Lottermoser (*ibid.* 1905, 71, 296); Chassevant (Bull. Soc. chim. 1904, 31, 11); Gutbier and Hofmeier (Zeitsch. anorg. Chem. 1905, 45, 77); Kohlschütter (Zeitsch. Elektrochem. 1908, 14, 49; Rebière, Compt. rend. 1912, 154, 1540; Pappadà, Zeitsch. Chem. Ind. Kolloide, 1911, 9, 265; Gans, Ann. Physik. 1915, [iv.] 47, 270).

The colour of colloidal silver varies very largely with the mode of preparation, and seems to be due to differences in the size of the colloidal particles, yellow solutions containing the smallest and blue solutions the largest particles. During the process of coagulation by dilute alkali, the colour of the solution changes gradually in the order yellow, red, green, blue; the substance has never been obtained absolutely pure and, according to Hanriot (Compt. rend. 1903, 137, 122), the different varieties are distinct chemical individuals, the 'impurity' forming an integral part of the molecule. Their colour is affected by light, but this change is said to be prevented by the addition of certain organic liquids (Gallagher, J. Phys. Chem. 1906, 10, 701). All forms of the solid are brittle, easily powdered, amalgamate with mercury, and are instantly converted by acids into normal grey silver, without evolution of gas.

Colloidal silver is sometimes known as *collargol* in therapeutics, but this name (according to Hanriot, *l.c.*) should only be applied to those forms which contain albuminoid matter, or a certain characteristic grouping (Danlos and Cothureau, J. Soc. Chem. Ind. 1903, 315, 514; Hanriot, Compt. rend. 1903, 136, 680, 1448).

Gerasimov (J. Russ. Phys. Chem. Soc. 1916, 48, 87, 251) gives the following as the best method of preparing collargol. The reducing mixture is obtained by shaking 100 grms. of albumin with a solution of 15 grms. of sodium hydroxide in 500 c.c. of water until uniformly distributed, when the liquid is heated and filtered. To 27–30 grms. of this solution is added the silver oxide obtained by precipitating 10 grms. of silver nitrate with potassium hydroxide. The mixture is diluted to 200 c.c. and heated on the

water-bath with constant shaking for an hour. When cold a few drops of acetic acid are added and the precipitate after washing is dissolved in the minimal quantity of sodium hydroxide. The liquid, after settling, is evaporated over sulphuric acid or in a vacuum at about 40°. The blue powder thus obtained contains about 75 p.c. of silver.

Colloidal silver is used in medicine, chiefly for the preparation of Credé's ointment (*Unguentum Credé*), which is composed of 15 parts colloidal silver, 5 of water, 10 of white wax, and 70 of benzoated lard. The ointment is used in the treatment of various forms of septic infection.

Preparations containing colloidal silver or silver oxide are prepared by treating aqueous solutions of silver salts with an alkaline solution of a tannin (*e.g.* catechu, catechin, kino, &c.), which yield protocatechuic acid and phloroglucinol when fused with potassium hydroxide. The colloidal solutions so formed are freed from alkali and salts by dialysis and then evaporated to dryness in a vacuum. The products are soluble in water and possess the antiseptic properties of colloidal silver and the astringent properties of tannin substances (D. R. P. 208189).

Odén (Zeitsch. physikal. Chem. 1912, 78, 682) has employed the method of fractional coagulation to the separation of silver hydrosols into fractions of different degrees of dispersion. The yellow and red hydrosols contain only amicroscopic particles; the purple and lilac sols. contain submicrons. Quince seed extract may be used as a protective colloid in the preparation of colloidal silver (Gutbier and Wagner, Kolloid. Zeitsch. 1916, 19, 280). Colloidal silver may also be obtained by reducing silver oxide with a 60 p.c. solution of formaldehyde at 35°. The solution which varies in colour from pale lilac to rich ruby red is stable. The colour is discharged slowly by salt solutions and by nitric acid (Pickles, Chem. News, 1918, 117, 358).

Schaum and Lang (Kolloid Zeitsch. 1921, 28, 243) state that for transmitted light the diameters of the particles of colloidal silver associated with the following colours are: yellowish-orange 60 $\mu\mu$; orange-red, 90 $\mu\mu$; purple, 120 $\mu\mu$; violet, 150 $\mu\mu$; and bluish-green, 180 $\mu\mu$.

An exceedingly stable and concentrated silver solution may be prepared by reducing with hydrazine 10 parts of *N*/10 silver nitrate in 30 parts of 0.42 p.c. gelatin solution, and immediately dialysing for 6 hours. This solution is reddish-brown by transmitted light, and olive by reflected light. After dialysing for 10 days it contained 40.45 p.c. of silver and was stable for nine months (Gutbier, Huber, and Zweigle, Kolloid Zeitsch. 1922, 30, 306).

Measurements of the electrical conductivity of silver sols, prepared by the reduction of an ammoniacal solution of silver chloride by dilute hydrazine hydrate solution, have been carried out with the dialysed sol. The minimum precipitating values of potassium nitrate, silver nitrate, sulphuric acid, barium nitrate, and mercuric chloride have been found for the dialysed sol, and analyses of the coagulum and the filtrate made. The results indicate that

unprotected colloidal silver has the composition and constitution represented by



(Paul Neureiter and Wo. Pauli, *Kolloid Zeitsch.* 1923, 33, 67-73; *J. Chem. Soc.* 1923, 123, 124, ii. 636).

After electrolysis of dilute aqueous sodium or potassium hydroxide or sulphuric acid, the cathode liquid has the property of reducing an alkaline silver solution. The reducing agent is unstable, one-half disappearing in a day, and is shown not to be ferrous hydroxide or active hydrogen (G. Tammann, *Zeitsch. anorg. Chem.* 1923, 126, 176).

A catalytically active form of silver is obtained by reducing a solution of silver perchlorate with a solution of chromous acetate in perchloric acid solution. It is twice as active as so-called 'molecular' silver (from the action of zinc on silver chloride) in promoting the reaction $2\text{CrCl}_2 + 2\text{HCl} = 2\text{CrCl}_3 + \text{H}_2$. The catalytic silver is a white powder, d 1.7, and contains 99.6 p.c. Ag (*J. Picard and E. Thomas, Helv. Chim. Acta*, 1923, 6, 1044; *J. Soc. Chem. Ind.* 1924, 43, B. 99).

SILVER OXIDES AND SALTS.

Silver oxide Ag_2O is obtained as a brown, hydrated precipitate by addition of potash to silver nitrate, or as a bluish-black powder by boiling the precipitated chloride with concentrated potash. It is also formed in small quantities when silver is heated in air or oxygen at 500° - 550° (Berthelot, *Compt. rend.* 1900, 131, 1159).

Silver is volatilised at high temperatures and vaporises more easily in oxygen than in nitrogen, due probably to the formation of oxide (Ag_2O ?).

When dried at 60° - 80° the oxide becomes almost black. At ordinary temperature it is soluble in 15,360 parts of water (Levi, *Gazz. chim. ital.* 1901, 31, ii. 1; $2.16 + 10^{-4}$ gm.-mols. per litre at 25° , Rebière, *Bull. Soc. chim.* 1915, [iv.] 17, 309), the solution having an alkaline reaction and a metallic taste. Acids dissolve it, with production of salts, which are generally anhydrous. The recently precipitated moist oxide absorbs carbon dioxide from the air (Rose, *Pogg. Ann.* 85, 304). Hydrogen reduces silver oxide to metal at 100° . Tin and copper also reduce it in presence of water, and carbon monoxide reduces it in the dry state at ordinary temperature (Dejust, *Compt. rend.* 1905, 140, 1250). When heated at 250° it begins to decompose, and above 270° it rapidly loses its oxygen, which is entirely evolved at about 300° - 340° .

Silver oxide decomposes soluble chlorides with formation of silver chloride and precipitates the corresponding oxide from solutions of many metallic salts. When rubbed in a mortar with sulphur, phosphorus, antimony, or arsenic sulphides, or with any other readily oxidisable substance, ignition takes place.

Silver oxide dissolves in ammonia forming $\text{Ag}_2\text{O}\cdot 2\text{NH}_3$, but care should be taken in working with ammoniacal silver solutions as dangerous explosions may sometimes occur (Matignon, *Bull. Soc. chim.* 1908, [iv.] 3, 618; Sieverts, *Zeitsch. angew. Chem.* 1909, 22, 6). The ratio NH_3/Ag for solutions of silver oxide in aqueous ammonia

is constant up to a concentration of about 2 gm.-mols. of ammonia per litre, after which it increases slowly and regularly. The ratio decreases in course of time when a concentrated solution is kept in contact with silver oxide. An explanation is suggested based on the slow decomposition of the complex $\text{Ag}_2\cdot 2\text{NH}_3\cdot \text{OH}$ into silver amide in concentrated solution.

The ratio MeNH_2/Ag is constant for solutions containing less than 2 gm.-mols. of methylamine per litre; beyond this concentration it increases very rapidly, although the silver concentration passes through a maximum (0.96 gm.-atom of silver to 6.25 gm.-mols. of methylamine per litre). Some of the methylamine appears to be oxidised to formic acid. Anhydrous trimethylamine will not dissolve silver oxide (L. J. Olmer, *Bull. Soc. Chem.* 1924, [iv.] 35, 333; *Chem. Soc. Abstr.* 1924, 126, ii. 410).

Many acids and alcohols are oxidised by silver oxide in alkali hydroxide or ammoniacal solution. Hydroxylic aliphatic compounds must contain a $\text{:CH}\cdot\text{OH}$ (or CO or $\text{C}[\text{OH}]_2$) group combined with two $\text{CH}_2\cdot\text{OH}$, two $\text{:CH}\cdot\text{OH}$, or two CO_2H groups, or with any two of these three groups. Tartronic, tartaric, dihydroxy-tartaric, glyceric, mucic, saccharic, and gluconic acids, dextrose, glycerol, and mannitol are thus oxidised. For oxidation in neutral or acid solution, it suffices that the $\text{:CH}\cdot\text{OH}$ group shall be combined with a carboxyl group and also with H , CH_2 or CH_3 . Glycollic, lactic, malic, and formic acids are thus oxidised (Behrend and Dreyer, *Ann.* 1918, 416, 203; *Chem. Soc. Abst.* 1919, i. 64).

Silver oxide is used to impart a yellow colour to glass, one process being to dip the warm glass in a flux composed of 20-30 parts of sodium metaphosphate and 4 of silver nitrate, or in the case of small articles, a mixture of clay and silver oxide is applied to the surface and the article heated in a muffle. To obtain a metallic lustre, small quantities of silver nitrate are fused with the material for making glass, and while the melt is still hot the surface is reduced by being exposed to alcohol vapours (Zsigmondy, *Dingl. poly. J.* 1897, 306, 91, 68). It sometimes replaces the nitrate in medicine, as its discolouring action on the skin after prolonged internal use is much less; on the other hand, its slight solubility causes it to be of perhaps less benefit than the nitrate (*Nat. Standard Dispensatory*, 1905).

Colloidal silver oxide or hydroxide is said to be contained in an alkaline solution of silver protalbinat and lysalbinat (Paal, *Ber.* 1902, 35, 2206).

According to Bruce (*Chem. News*, 1884, 50, 208), the hydroxide $\text{Ag}_2(\text{OH})_2$, obtained by mixing dilute solutions of silver nitrate and potash in alcohol of 90 p.c. at -50°F ., is almost white. It, however, soon darkens, and is brownish even at -40°F . (see also *Fr. Pats.* 342865, 346066; Carnelly and Walker, *Chem. Soc. Trans.* 1888, 79; Lohnstein, *Chem. Zentr.* 1909, ii. 1533). It behaves as a very weak base.

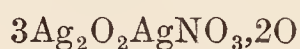
Silver oxide corresponds to the only well-defined series of silver salts, most of which are insoluble in water. The soluble salts have a neutral reaction and an unpleasant metallic taste, and are often poisonous (*Chem. Zentr.* 1908, i. 56; Izar, *Biochem. Zeitsch.* 1909, 20, 249, 266).

The silver salts are readily reduced by aldehydes, aromatic amines, and many other organic compounds (Morgan and Mickelthwaite, *J. Soc. Chem. Ind.* 1902, 1373). Their general stability is said to be increased by the addition of a thickening medium, such as gelatin (*Fr. Pat.* 321830, 1902).

Silver salts have been suggested for use in the sterilisation of drinking water; the pathological organisms of cholera, typhoid, and dysentery, are instantly destroyed by very small proportions of the disinfectant (*Traetta-Mosca, Gazz. chim. ital.* 1909, 39, i. 69).

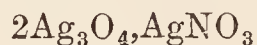
Silver peroxide. The body to which this name is usually applied was first obtained by Ritter in 1804 by the electrolysis of a silver nitrate solution (Berthelot, *Compt. rend.* 1880, 90, 653; *ibid.* 1901, 132, 897; *ibid.* 1901, 133, 555).

It was for a long time considered to have the composition Ag_2O_2 (Wallquist, *J. pr. Chem.* [i.] 31, 179; Fischer, *ibid.* 32, 108), but more recent analyses have shown that it contains nitrogen, and has the composition $\text{Ag}_7\text{NO}_{11}$ or



It is therefore termed *silver peroxy-nitrate* (Mulder and Heringa, *Rec. trav. chim.* 1896, 15, 1, 235; Mulder, *ibid.* 16, 57; *ibid.* 1903, 22, 235, 405; Sulc, *Zeitsch. anorg. Chem.* 1896, 12, 89, 180; *ibid.* 1900, 24, 305; Watson, *Chem. Soc. Trans.* 1906, 578; Barbieri, *Atti R. Accad. Lincei*, 1907, [v.] 16, ii. 72).

According to Baborovský and Kužma (*Zeitsch. physikal. Chem.* 1909, 67, 48), the silver peroxy-nitrate consists of the peroxide Ag_3O_4 , mixed with silver nitrate (Bose, *ibid.* 1909, 68, 383). Brown (*J. Phys. Chem.* 1916, 20, 680) finds that it has the formula

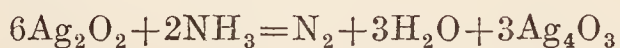


Cf. Weber, *Trans. Amer. Electrochem. Soc.* 1917, 32, 391. Similar peroxy salts are obtained by the electrolysis of other silver salts (Mulder, *Rec. trav. chim.* 1900, 19, 115; Tanatar, *Zeitsch. anorg. Chem.* 1901, 28, 331).

When silver peroxy-nitrate is treated with water it reacts thus,



The silver nitrate goes into solution, and the peroxide thus obtained (Watson, *l.c.*) is precipitated as a greyish-black powder, sp.gr. 7.44 (approximately), which may be heated to 100° without change. At a higher temperature it evolves oxygen and deposits silver. With ammonia it reacts thus

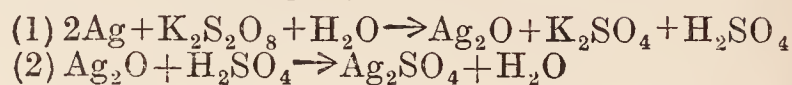


the latter oxide has, however, not been isolated (*see also* Berthelot, *l.c.*). *See also* Higson, *Chem. Soc. Trans.* 1921, 119, 2048.

Both the peroxy salts and the peroxide dissolve in cold, strong nitric acid, forming an intensely brown solution, and in strong sulphuric acid with an olive-green colour.

Silver peroxide is also said to be obtained by the action of potassium persulphate solution on silver nitrate or silver sulphate (Marshall, *Chem. Soc. Trans.* 1891, 771; *J. Soc. Chem. Ind.* 1897, 16, 396); Levi, Migliorini, and Ercolini (*Gazz. chim. ital.* 1908, 38, i. 583) have investigated the

action of persulphates on metallic silver, and give the following equations:—



(*cf.* Higson, *l.c.*), and by the action of ozone on silver. Possibly the oxide Ag_2O_3 also exists (Luther and Pokorny, *Zeitsch. anorg. Chem.* 1908, 57, 290).

Silver carbonate Ag_2CO_3 is obtained by precipitating silver nitrate with an alkaline carbonate as a white precipitate, which turns yellow on washing, and is blackened by light. It is said to lose the whole of its carbon dioxide at 200° (Colson, *Compt. rend.* 1905, 140, 865). A solution of the salt in ammonia gives, on addition of alcohol, a grey precipitate having the composition $\text{Ag}_2\text{CO}_3\cdot 4\text{NH}_3$. Dervin and Olmer (*Compt. rend.* 1921, 172, 1662) obtained ammoniacal silver carbonate by repeated spontaneous evaporation in air of ammoniacal solutions of silver oxide. The crystals had the composition $\text{Ag}_2\text{CO}_3\cdot 4\text{NH}_3\cdot \text{H}_2\text{O}$; exposed to the air they lose water and ammonia.

According to G. S. Johnson (*Chem. News*, 1886, 54, 75), silver carbonate is obtained in crystals by dissolving the precipitated carbonate in water saturated with carbon dioxide at 15°. He has also obtained it in large glistening yellow prisms, which melt at low redness and decompose at a somewhat higher temperature with evolution of carbon dioxide, by exposure of the oxide in presence of water to the air for 2 months. Schulten (*Compt. rend.* 1887, 105, 881) has obtained a white precipitate which changes to microscopic crystals of the composition AgKCO_3 , by the addition of silver nitrate to a concentrated solution of potassium carbonate containing free carbon dioxide. Water decomposes the crystals, with formation of the normal carbonate (Reynolds, *Chem. Soc. Trans.* 1898, 265).

Colloidal silver carbonate can be obtained by adding silver nitrate to sodium proto- or lys-albinate and dissolving the silver-albinate so obtained in sodium carbonate and dialysing the solution (D. R. P. 175794). This can be employed as a general method for the preparation of colloidal silver compounds, such as the phosphate, sulphide and the halides (Paal and Voss, *Ber.* 1904, 37, 3862).

Silver nitrate AgNO_3 is usually prepared by dissolving silver in nitric acid, and is largely so obtained in the 'parting' of silver from gold by nitric acid. The salt may be freed from copper by boiling with freshly precipitated silver oxide, which precipitates the copper as oxide; or by heating the fused salt until the copper nitrate has been decomposed, which occurs before the silver salt is affected. When a portion dissolved in water and treated with ammonia gives no blue colour, the mass is cooled, dissolved in water, filtered from the copper oxide, and recrystallised. In working up photographic and other silver residues, the chloride produced from solutions by addition of hydrochloric acid, and the ash of papers, &c., is mixed with 4 or 5 times its weight of sodium carbonate or of a mixture of potassium and sodium carbonates, and is heated in a crucible to bright redness, when the silver collects as a button in the bottom of the crucible. The precipitated

chloride may also be reduced by zinc or iron in water slightly acidulated with hydrochloric or sulphuric acid.

Silver nitrate crystallises in colourless rhombic tables of sp.gr. 4.328 (Schröder, Pogg. Ann. 106, 226), melting at 218° (Carnelley, Chem. Soc. Trans. 1878, 276), and resolidifying to a fibrous crystalline mass. According to Guinchant it melts at 209° (Compt. rend. 1909, 149, 569). At 159° it passes from the monoclinic to the orthorhombic form. When the fused salt is cast in sticks, it forms the *lunar caustic* of pharmacy (Warden, Pharm. J. 1897, 58, 61). At a heat much below redness it is decomposed into silver nitrite, with evolution of oxygen, and at a red heat into silver, nitrogen peroxide, oxygen, and nitrogen. According to Colson it commences to decompose at 350° (Compt. rend. 1909, 148, 738; Divers, Chem. Soc. Trans. 1899, 83).

Water dissolves the nitrate with formation of a neutral solution; hot alcohol dissolves about a fourth of its weight; strong nitric acid has but little solvent action. According to Kremers (Pogg. Ann. 92, 497) its solubility in 100 parts of water is:—

0°	19.5°	54°	85°	110°
121.9	227.3	500	714	1111

(see also Landolt Börnstein, Tabellen, 1905, 520).

Tilden and Shenstone (Phil. Trans. 175, 33) find that 100 parts of water at 125° dissolve 1622.5 parts, and at 133° no less than 1941.4 parts of the salt.

Dry silver nitrate absorbs ammonia, with evolution of sufficient heat to fuse it, and production of a compound of the formula $\text{AgNO}_3 \cdot 3\text{NH}_3$ (Rose, Pogg. Ann. 20, 153). Ammonia nitrates of the composition $\text{AgNO}_3 \cdot \text{NH}_3$ (Reychler, Ber. 16, 992, and 2421) and $\text{AgNO}_3 \cdot 2\text{NH}_3$ (Mitscherlich, Pogg. Ann. 9, 413; and Marignac, Ann. Min. [v.] 15, 25), have also been prepared.

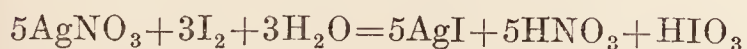
Silver ammonio-nitrate $\text{Ag}(\text{NH}_3)_2\text{NO}_3$ is obtained in white acicular crystals by treating a strong aqueous solution of 5 grms. silver nitrate in 4–5 c.c. of water with a concentrated solution of ammonia until the precipitate first formed is almost redissolved and a faintly opalescent liquid is obtained. This is filtered and 120 c.c. of alcohol is added when the crystals separate out. If ether is used instead of alcohol the salt is obtained in the amorphous state (Castoro, Gazz. chim. ital. 1907, 37, i. 310; Lüppe Cramer, Chem. Zeit. 1904, 28, Rep. 296). For the probable existence of a mono-ammoniacal silver nitrate v. Reychler, Bull. Soc. chim. Belg. 1914, 28, 198.

Double nitrates of the composition $\text{AgNO}_3 \cdot \text{KNO}_3$; $\text{AgNO}_3 \cdot \text{RbNO}_3$; and $\text{AgNO}_3 \cdot \text{NH}_4\text{NO}_3$ have been obtained by Ditte (Compt. rend. 1885, 101, 878; see also Rose, l.c.).

Silver nitrate forms fairly stable salts with asparagine, carbamide, urethane, leucine, and other amino-derivatives (Castoro, l.c.).

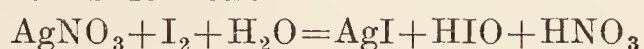
It also forms other additive organic compounds (Scholl and Steinkop, Ber. 1906, 39, 4393).

With iodine silver nitrate reacts thus



(Pawloff and Schein, J. Russ. Phys. Chem. Soc. 1907, 39, 943). According to H. S. Taylor

(Chem. Soc. Trans. 1913, 103, 31) hypiodous acid is first formed:



the hypiodous acid in presence of soluble silver salts being converted into iodide and iodate:



(cf. Normand and Cumming, Chem. Soc. Trans. 1912, 101, 1852).

Senderens (Compt. rend. 1887, 104, 175, and 504) has examined the action of zinc, lead, tin, and aluminium, and of selenium, tellurium, arsenic, phosphorus, iodine, and bromine on aqueous silver nitrate.

Silver nitrate is used as a marking-ink and as a constituent of certain hair dyes, and is very largely employed in photography. It is used in medicine both externally and internally (v. Squire's Companion to the British Pharmacopœia, 1890, 79, and the U.S. Dispensatory, 1879, 1088; Nat. Stand. Dispensatory by Hare Caspari, &c., 1905; Pigorini, Atti R. Accad. Lincei, 1907, v. 16, i. 359). It is also used in chemical analytical work.

Thermal studies of the systems formed by silver nitrate with mercuric iodide show that no double decomposition occurs, but the following compounds are formed: $2\text{AgNO}_3 \cdot \text{HgI}_2$, yellowish-green crystals, m.p. 107°; $\text{AgNO}_3 \cdot \text{HgI}_2$, m.p. 117°–118°, undergoing at 52° dimorphic change marked by change of colour from canary-yellow to orange (A. G. Bergmann, J. Russ. Phys. Chem. Soc. 1921, 53, 181).

An unstable *pernitrate* AgNO_4 has been obtained by Baborovský and Kužma, Zeitsch. Elektrochem. 1908, 14, 196).

Silver nitrite AgNO_2 is best obtained by precipitating silver nitrate solution with potassium nitrite (V. Meyer, Annalen, 1874, 171, 23). It forms a white crystalline powder, difficultly soluble in cold water. The percentage solubility is at 1°, 0.1589; at 15°, 0.2752; at 25°, 0.4135; at 35°, 0.6016; at 51°, 1.0240; at 60°, 1.3625 (Creighton and Ward, J. Amer. Chem. Soc. 1915, 37, 2333). From hot solution it separates in yellowish needles or prisms. It does not melt but decomposes freely at 180° (Divers, Chem. Soc. Proc. 1905, 281).

With iodine in carbon tetrachloride it gives a quantitative yield of nitrogen peroxide (Neelmeier, Ber. 1904, 37, 1386).

Triple nitrites with caesium, lead, strontium, and potassium have been prepared (Jamieson, Amer. Chem. J. 1907, 38, 614), and a double nitrite with cobalt by Cunningham and Perkin (Chem. Soc. Trans. 1909, 1568).

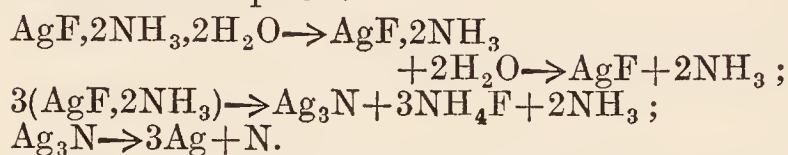
Silver hyponitrite $(\text{AgON})_2$ is a bright yellow salt stable at 100°, but decomposing in air when moist, thus: $2(\text{AgON})_2 = 4\text{Ag} + \text{N}_2 + 2\text{NO}_2$; $4\text{NO}_2 + (\text{AgON})_2 = 2\text{AgNO}_3 + 4\text{NO}$ (Divers, J. Soc. Chem. Ind. 1899, 274; Kirschner, Zeitsch. anorg. Chem. 1898, 16, 424).

Silver nitride Ag_3N , or Berthelot's *fulminating silver*, is obtained when freshly precipitated oxide is dissolved in ammonia and the solution exposed to the air (Crell's Annalen, 1788, 2, 390; Raschig, Annalen, 1886, 233, 93).

It forms a black powdery precipitate or black lustrous crystals. When dried, it explodes violently on the slightest friction; in fact, explosion frequently occurs even under water. Acids convert it into ammonia and silver salts.

It is often mixed with metallic silver, and sometimes contains hydrogen, when it corresponds to the formula NHAg_2 . A yellow nitride of silver is said to be formed by heating together silver nitrate and magnesium nitride in a sealed tube (Smits, *Rec. trav. chim.* 1896, 15, 135). A number of ammoniates of silver salts have been described by Bruni and Levi (*Gazz. chim. ital.* 1916, 46, ii. 17). The general method of preparation consisted in absorption of dry ammonia by the dry salt; in precipitating ammoniacal alcoholic solutions of the salt by ether, or in evaporating aqueous ammoniacal solutions.

When silver ammonium fluoride is heated below 160° it decomposes, leaving a black residue of silver nitride, which is more sensitive to friction than to rise of temperature; it detonates at about 165° , but can be heated safely for several hours at 120° if agitation or rubbing be avoided. Silver nitride may also be obtained by keeping crystals of silver ammonium fluoride in a vacuum over sulphuric acid for eight months, treating with water, and filtering off the insoluble nitride. The latter dissolves in ammonia (7.5 grm.-mols. per litre) to the extent of 0.3 grm.-atom of silver per litre. During the desiccation of the silver ammonium fluoride four simultaneous reactions take place:

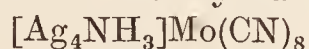


Ammonia catalyses the conversion of the double fluoride to nitride, it decomposes the nitride, and it hinders the volatilisation of the ammonium fluoride (L. J. Olmer and Dervin, *Bull. Soc. Chim.* 1924, 35, 152; *J. Soc. Chem. Ind.* 1924, 43, B. 418).

Silver amide AgNH_2 is formed by adding a solution of potassamide in liquid ammonia to an excess of silver nitrate in the same solvent. It is white, is soluble in liquid ammonia, and in ammonium salt solutions, darkens on exposure to light and explodes readily when dry (Franklin, *J. Amer. Chem. Soc.* 1903, 25, 827).

Silver azoimide AgN_3 forms minute crystals insoluble in water and very explosive. It is obtained by adding silver nitrate to an azoimide solution. It is highly sensitive to light, decomposition occurring with evolution of nitrogen and formation of metallic silver. No sub-compound is formed. Hence by analogy, Lothar Wöhler and Krupko (*Ber.* 1913, 46, 2045) infer that the photochemical alteration in the silver haloid of a photographic plate is due to an adsorption compound of finely-divided metal with unchanged haloid, and not to various subhaloids of different colours.

A molybdenum silver cyanamine



is described by Rosenheim (*Zeitsch. anorg. Chem.* 1909, 65, 166).

Silver cyanide AgCN is obtained as a white, curdy precipitate by addition of a soluble cyanide to silver nitrate solution. It dissolves readily in ammonia and soluble cyanides, and when heated with water or caustic potash is reduced to silver (Marsh and Struthers, *Chem. Soc. Proc.* 1902, 249). Sulphuric, hydrochloric, or boiling nitric acid decomposes it with evolution of

hydrocyanic acid (Plimmer, *Chem. Soc. Trans.* 1904, 12).

The ammoniacal solution contains the compound $\text{AgCN} \cdot \text{NH}_3$, while the cyanide solutions contain double cyanides, such as $\text{AgCN} \cdot \text{KCN}$; $\text{AgCN} \cdot \text{NaCN}$; $3\text{AgCN} \cdot 2\text{KCN} \cdot \text{NaCN}$ (Baup, *Ann. Chim.* 1852, [iii.] 53, 462). The double cyanide of silver with a heavy metal is best obtained by addition of silver potassium cyanide to a solution of a salt of the metal. Silver potassium cyanide, which is employed in the electroplating bath (*v. ELECTROPLATING*), crystallises in regular octahedra, soluble in 4 parts of water at 20° , and in 25 parts of alcohol of 85 p.c. at 20° (Baup, *l.c.*; see also Bailar, *J. Soc. Chem. Ind.* 1910, 1085).

Silver cyanate AgCNO is a white, somewhat soluble powder, which explodes on heating. It may be obtained by the addition of silver nitrate to potassium cyanate solution.

Silver thiocyanate AgSCN is a white, curdy precipitate readily soluble in ammonia.

Silver thiocyanate dissolves in potassium cyanide solution with quantitative formation of the complex salt $[\text{Ag}(\text{CN} \cdot \text{S})(\text{CN})_2]\text{K}_2$. On adding silver nitrate solution, this salt is decomposed with formation of $[\text{Ag}(\text{CN})_2]\text{K}$, and the silver thiocyanate is reprecipitated. The silver thiocyanate to be determined is stirred with water in a beaker standing on a black slab, and completely dissolved by the addition of a measured volume of standard potassium cyanide solution. Standard silver nitrate solution is then run in until the appearance of opalescence due to the reprecipitation of the thiocyanate. The weight of the latter is then calculated from the volumes of the two standard solutions used. The method gives accurate results, but fails in presence of halogen salts and cyanides, which set up equilibria with the silver thiocyanate (R. Cernatesco, *Ann. Sci. Univ. Jassy*, 1923, 11, 302–306; *Chem. Zentr.* 1923, 94, iv. 633–634; *J. Soc. Chem. Ind.* 1923, 42, 1129, A).

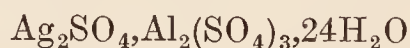
Potassium silver thiocyanate $\text{AgK}(\text{SCN})_2$, formed when silver thiocyanate is dissolved in potassium thiocyanate, melts at 140° , and is decomposed by water.

Silver sulphate Ag_2SO_4 may be obtained by dissolving the metal in concentrated sulphuric acid or by dissolving the oxide or carbonate in the acid. It dissolves easily in sulphuric or nitric acid, but requires about 200 parts of cold or 68.58 parts of hot water for solution (Kremers, *Pogg. Ann.* 92, 499).

Silver sulphate crystallises in small rhombic prisms isomorphous with anhydrous sodium sulphate (Mitscherlich, *ibid.* 12, 138), and fusing at 654° (Carnelley, *Chem. Soc. Trans.* 1878, 279).

For the dissociation of silver sulphate under the influence of heat, see Marchal (*Compt. rend.* 1923, 176, 299).

An acid salt HAgSO_4 crystallising in pale-yellow prisms, and a double sulphate with aluminium (silver alum)



(Church, *Chem. News*, 1864, 9, 155) are also known. The latter salt crystallises in octahedra, which are decomposed by water into the component sulphates.

Silver sulphate also forms double salts with tin and antimony sulphates (Weinland and Kühl, *Zeitsch. anorg. Chem.* 1907, 54, 244, 256).

According to Carey Lea (*Amer. J. Sci.* 1892, 44, 322) the double salt $\text{Ag}_4\text{SO}_4, \text{Ag}_2\text{SO}_4, \text{H}_2\text{O}$ is produced when silver nitrate is reduced with hypophosphorous acid in presence of sulphuric acid. It forms a pale-brown powder which, however, cannot be wholly purified from phosphoric anhydride.

Silver persulphate. Silver nitrate dissolved in pyridine added to a cold solution of potassium persulphate yields golden yellow microscopic needles of a compound containing bivalent silver and of the composition $\text{AgS}_2\text{O}_8, 4\text{Py}$, unchanged in diffused light, reduced by dilute ammonia solution and decomposed by dilute acids or sodium hydroxide solution (Barbieri, *Gazz. chim. ital.* 1912, 42, ii. 7).

Silver sulphite Ag_2SO_3 is obtained in small, white glistening needles, or as a white curdy precipitate, by dissolving silver oxide in sulphurous acid and crystallising, or by precipitating a silver salt with sulphurous acid or a sulphite. Several double alkaline sulphites are known.

Silver sulphite and the alkali silver sulphites, when boiled with water or heated at 100° , are converted into dithionates and only after raising the temperature do they decompose, forming sulphur dioxide and silver sulphate (Baubigny, *Compt. rend.* 1909, 149, 735, 858).

Silver thiosulphate or hyposulphite $\text{Ag}_2\text{S}_2\text{O}_3$ is obtained as a snow-white, slightly soluble powder, of sweetish taste, by addition of dilute silver nitrate to excess of concentrated sodium thiosulphate (*v.* Herschel, *Edin. Phil. J.* 1819, 1, 26 and 2, 154). It forms double salts with the alkali metals (Richards and Faber, *Amer. J. Sci.* 21, 167; Rosenheim and Steinhauser, *Zeitsch. anorg. Chem.* 1900, 25, 72; Gädicke *Zeitsch. angew. Chem.* 1903, 16, 608). The salt NaAgS_2O_3 is obtained by evaporating a solution of silver chloride in sodium thiosulphate, or better by adding a neutral solution of silver nitrate to a solution of sodium thiosulphate until a permanent precipitate is formed, after which the solution is filtered and alcohol is added. The salt is thus precipitated in silky laminæ.

The ammoniacal solution of this salt may be used for silvering. Cohen (*Chem. Soc. Trans.* 1887, 39) has described a thiosulphate of the composition $\text{Ag}_2\text{S}_2\text{O}_3, 2\text{K}_2\text{S}_2\text{O}_3$.

Silver sulphide Ag_2S occurs native in *argentite*, *vitreous silver*, or *silver glance*. As double sulphide, it occurs as red silver ore $3\text{Ag}_2\text{S}, \text{Sb}_2\text{S}_3$. It may be obtained by heating silver chloride in a current of sulphuretted hydrogen, by heating silver with sulphur or sulphuretted hydrogen, or by precipitating silver solutions with sulphuretted hydrogen.

The blackening of metallic silver by hydrogen sulphide or soluble sulphides only takes place in presence of air or oxygen (Hahn, *Zeitsch. anorg. Chem.* 1917, 99, 118).

Silver sulphide melts at 812° when pure (Friedrich, *J. Soc. Chem. Ind.* 1908, 403). It is sufficiently soft to be cut with a knife, and fuses readily without change, but when roasted in the air becomes gradually converted into silver. It is decomposed by boiling strong

sulphuric, nitric, or hydrochloric acid (Gruener, *J. Amer. Chem. Soc.* 1910, 32, 1030), and is converted into the chloride by digestion with cuprous chloride solution. The presence of sodium chloride facilitates the latter reaction, which is employed for removing silver from certain ores by dissolving the silver chloride as fast as formed.

A mixture of silver sulphide and silver sulphate in molecular proportions forms a viscous dark red-brown fluid at 365° , which imparts to glass immersed in it a dark-brown colour, the shade depending on the duration of immersion. The glass so coloured is opaque to blue and ultra-violet rays, and may be used for photographic purposes.

Silver sulphide forms double salts with other metallic sulphides.

Silver disulphide Ag_2S_2 is obtained by mixing a solution of silver nitrate in benzonitrile with a solution of sulphur in carbon disulphide. It is a brown amorphous powder insoluble in all ordinary solvents. Heated in a test-tube it melts and then decomposes. It is also decomposed by hydrochloric and by nitric acids (Hantzsch, *Zeitsch. anorg. Chem.* 1899, 19, 104).

Silver sub-sulphide *v.* *Silver sub-salts*, &c.

Silver selenide Ag_2Se is a dark-grey body, which melts at 834° – 850° (897° Pellini) to a silvery mass (Friedrich and Leroux, *Metallurgie*, 1908, 5, 355). It is obtained by heating silver with selenium, or by precipitating a silver solution with seleniuretted hydrogen. A diselenide Ag_2Se_2 is also known. Selenides of silver and lead (*naumannite*) and of silver and copper (*eukarite*) occur in nature; double compounds with antimony and bismuth are described by Pélabon (*Compt. rend.* 1908, 146, 975; Pellini, *Gazz. chim. ital.* 1915, 45, i. 533).

Silver chromate Ag_2CrO_4 is obtained in dark-red crystals by the addition of potassium chromate solution to silver nitrate. It dissolves in alkaline chromates and in the nitrates of ammonia and the alkalis (R. F. Carpenter, *J. Soc. Chem. Ind.* 1886, 286; and Biscaro, *Chem. News*, 1886, 53, 67; Baxter, *J. Amer. Chem. Soc.* 1909, 31, 529, 541).

When the red salt is dissolved in dilute acetic acid and the solution is concentrated, a greenish-blue modification is formed (Margosches, *Zeitsch. anorg. Chem.* 1906, 51, 231). By precipitating silver chromate in the presence of albuminous substances, a colloidal form of the salt is obtained (D. R. P. 166154; *Chem. Zentr.* 1906, i. 617).

By cooling a hot ammoniacal solution of silver chromate yellow crystals of $\text{Ag}_2\text{CrO}_4, 4\text{NH}_3$ are obtained.

Silver thiochromate and double salts of the chromate with phosphoric anhydride and other compounds are known. Possibly potassium silver chromate may exist (Gröger, *ibid.* 1907, ii. 516).

Silver chromate has been employed in miniature painting.

Silver dichromate $\text{Ag}_2\text{Cr}_2\text{O}_7$ is obtained in dark, reddish-brown, triclinic prisms, somewhat soluble in water, by precipitating a boiling solution of silver nitrate, acidified with nitric acid, with potassium dichromate solution (Autenrieth, *Ber.* 1902, 35, 2057; Mayer, *ibid.* 1903, 36, 1740; Baxter, *l.c.*).

Silver phosphates. Several phosphates are

known. The normal *orthophosphate* Ag_3PO_4 is obtained as a lemon-yellow powder, insoluble in water, but readily soluble in acids and ammonia, by precipitating a silver nitrate solution with an orthophosphate. It may be obtained in rhombic dodecahedra (Joly, Compt. rend. 1886, 103, 1071). It fuses at about 849° (Carnelley, Chem. Soc. Trans. 1878, 280). The *diargentic phosphate* Ag_2HPO_4 may be obtained in colourless hexagonal prisms (Joly, *l.c.*), which become yellow in contact with water or alcohol, with decomposition into the normal salt and phosphoric acid. *Silver pyrophosphate* $\text{Ag}_4\text{P}_2\text{O}_7$ is obtained as a white precipitate by addition of sodium pyrophosphate to silver nitrate. It fuses at 585° (Carnelley, *l.c.*) to a brown liquid, which re-solidifies to a white mass of radiating crystals. It is soluble in ammonia, from which it is precipitated unchanged by acids. The *dihydrogen pyrophosphate* $\text{H}_2\text{Ag}_2\text{P}_2\text{O}_7$ is formed by heating the pyrophosphate with aqueous phosphoric acid. It is a white powder, m.p. 240° (Cavalier, Compt. rend. 1904, 139, 284). The *metaphosphate* $\text{Ag}_2\text{P}_2\text{O}_6$ or AgPO_3 is obtained as a crystalline powder, slightly soluble in water, and fusing at 482° (Carnelley, *l.c.*) to a transparent glass, by precipitating silver nitrate with sodium metaphosphate.

Colloidal silver phosphate is obtained by adding silver nitrate to a solution of sodium phosphate and sodium protalbinat (D. R. P. 175794; Paal and Voss, *l.c.*).

A silver phosphate emulsion for photographic purposes is prepared by adding a large excess of disodium phosphate to a solution of silver nitrate and gelatin. Potassium chlorate, citric acid, and, if necessary, chrome alum are then added (Fr. Pat. 378305, 1907).

A number of silver nitrogen phosphates (Stokes, Amer. Chem. J. 1894, 16, 137; *ibid.* 1896, 18, 646, 658; *ibid.* 1898, 20, 757), and silver thiophosphates (Ferrand, Ann. Chem. 1899, [vii.] 17, 388; Glatzel, Zeitsch. anorg. Chem. 1893, 4, 215) have been prepared.

Silver phosphites and hypophosphites are also known (Sänger, Annalen, 1885, 232, 14; Gutbier, Zeitsch. anorg. Chem. 1902, 32, 350).

Silver biphosphide AgP_2 is obtained by passing phosphorus vapour over finely divided silver or silver chloride at 400° (Granger, Compt. rend. 1897, 124, 896). A number of other phosphides are described in earlier literature, but it is doubtful whether they exist.

Silver arsenate Ag_3AsO_4 is a dark-red, crystalline powder obtained by the addition of boiling silver nitrate solution to concentrated arsenic acid or to an arsenate. A silver arsenate $\text{Ag}_3(\text{AsO}_4)_2$ is described by Scagliarini and Guida (Gazz. chim. ital. 1914, 44, i. 574). The silver mercury compound $\text{AgHg}_2\text{AsO}_4$ is described by Jacobsen (Bull. Soc. chim. 1909, [iv.] 5, 947).

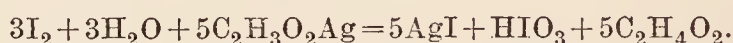
Silver arsenite Ag_3AsO_3 is a canary-yellow powder. Its ammoniacal solution when boiled deposits silver. Other arsenates and arsenites, as well as similar compounds with antimony, tellurium, lead, and other metals are known.

When stibine is washed, dried, and passed into a cold $N/2$ -solution of silver nitrate, pure silver antimonide is deposited (E. J. Weeks and W. V. Lloyd, Chem. News, 1923, 127, 362; Chem. Soc. Abstr. 1924, 126, ii. 43).

Silver plumbite PbO_2Ag_2 is obtained by adding silver nitrate solution made alkaline with potash and to which ammonia has been added, to an excess of lead nitrate. It forms brown crystals, sp.gr. 8.60, which become greyish-black on heating without losing their lustre, form, or general properties; it is insoluble in water, ammonia, or caustic potash, soluble in hot acetic, and fairly so in cold nitric, acid. It yields an olive-green powder and gives a black streak (Bullnheimer, Ber. 1898, 31, 1287).

SILVER AND THE HALOGENS.

The halogens react with silver salts to yield an insoluble silver halide, an acid, and one or more oxidation products of either the acid or the halide. A typical case is the action of iodine on silver acetate:



The reactions on account of secondary oxidation are sometimes more complex. The oxidation reactions are more marked with chlorine and bromine than with iodine (Normand and Cumming, Chem. Soc. Trans. 1912, 1852).

Silver chlorides. Two chlorides are said to exist, the normal salt AgCl and the sub-chloride Ag_2Cl (?). Peculiar compounds which appear to be combinations of the normal and sub-chloride, and which are known as photochlorides, are also known. Regarding them and the sub-chloride, and the action of light on silver salts, *v. Silver sub-salts*, &c.

The normal silver chloride occurs in *horn silver* or *cerargyrite*, and as the double chloride and bromide of silver in *embolite*. It is obtained by the action of chlorine or hydrogen chloride on silver, or as a dense, curdy, white precipitate, which gradually becomes powdery, by addition of hydrochloric acid or a soluble chloride to silver nitrate solution. Heat of formation 30,500 cal. Silver chloride assumes a yellow colour when heated, has sp.gr. 5.5, and melts at 460° (Carnelley, Chem. Soc. Trans. 1878, 278; Ramsay and Eumorfopoulos, Phil. Mag. 1896, [v.] 41, 360). It solidifies to a soft, tough, horny mass, having a sp.gr. of 5.594 (Schröder, Pogg. Ann. 106, 226). According to Kohlrausch, the electric conductivity of silver chloride exceeds that of the bromide or iodide, and when fused exceeds that of sulphuric acid. *See also* Böttger (Zeitsch. physikal. Chem. 1906, 56, 83); Le Blanc and Kerschbaum (Zeitsch. Elektrochem. 1910, 16, 242, 680). At a white heat silver chloride volatilises.

The fused chloride is not appreciably soluble in cold water, although very slightly soluble in hot water (Stas, Compt. rend. 1871, 73, 710; Böttger, *l.c.*; Drucker, Zeitsch. Chem. Ind. Kolloide, 1909, 4, 216; Glówezyński, Koll. Chem. Beihefte, 1914, 6, 147). According to van Rossern (Chem. Weekblad. 1912, 9, 203) the mean values found by Ostwald's E.M.F. method are: at 18° 1.019×10^{-5} , and at 25° 1.429×10^{-5} gram-equivalents AgCl per litre. The precipitated chloride is more soluble, and the washings become cloudy on addition of either hydrochloric acid or silver nitrate. Silver chloride is slightly soluble in silver nitrate solution, in amount depending upon the concentration and temperature of the silver nitrate solution.

(Lowry, Proc. Roy. Soc. 1914, [A] 91, 53). In concentrated hydrochloric acid its solubility is about 1 in 200, and in the acid diluted with its own volume of water 1 in 600. It is much more soluble in alkaline chlorides, especially sodium chloride. The tendency of silver halides to form complexes with alkali halides increases from the chloride to the iodide and increases also with the electropositive character of the alkali metal, which functions as a simple ion of the complex (Barlow, J. Amer. Chem. Soc. 1906, 28, 1446; Forbes, J. Amer. Chem. Soc. 1911, 33, 1937; Thiel, J. Amer. Chem. Soc. 1915, 37, 508; Hill, *ibid.* 510). It dissolves readily in ammonia, forming $\text{Ag}(\text{NH}_3)_2\text{Cl}$ (Bodländer and Fittig). Pure strong nitric acid at 15° – 17° dissolves the precipitated chloride to the extent of 2.01 parts in 100,000 (Thorpe, Chem. Soc. Trans. 1872, 453). For the influence of nitric acid on the solubility of silver chloride in mercuric nitrate solution, see Buttle and Hewitt (*ibid.* 1908, 1405). Freshly precipitated silver chloride is soluble in a dilute aqueous solution of mercuric sulphate. No precipitate is formed on adding hydrochloric acid to a solution of silver sulphate and mercuric sulphate or nitrate or acetate (Finzi, Gazz. chim. ital. 1911, 41, ii. 538). Soluble thiosulphates and sulphites (*cf.* Luther and Leubner, Zeitsch. anorg. Chem. 1912, 74, 389), and ferric chloride also dissolve it, and potassium cyanide converts it into a soluble double cyanide AgCN, KCN , together with potassium chloride. It dissolves readily in coniine (Blyth, *ibid.* 1849, 350) and in solution of methylamine (Wurtz, Ann. Chim. [iii.] 30, 453). Silver chloride is slowly decomposed by boiling concentrated sulphuric acid (Sauer, Zeitsch. anal. Chem. 1873, 376). For the crystal structure of silver chloride, as well as of the other silver haloids, see Wilsey, Phil. Mag. 1921, [vi.] 42, 262.

Silver chloride is not reduced by carbon, but may be reduced by fusion with 4 or 5 times its weight of sodium carbonate, or of a mixture of sodium and potassium carbonates. Iron, zinc, and other oxidisable metals reduce it in presence of water, especially when acidified with hydrochloric acid.

Silver chloride is more readily reduced than the bromide (Liesegang, Chem. Zeit. 1901, Rep. 372). It reacts with hydrogen, forming silver and hydrochloric acid (Jouniaux, Compt. rend. 1901, 132, 1270, 1558).

Optically clear crystals of silver chloride become more or less opaque and dark in colour when exposed to a beam of light. The surface at which the beam enters becomes brown and particles visible in the ultra-microscope become visible. The particles grow rapidly and continue to grow if the crystal is removed from the light and heated at 350° . The effect is evidently due to the separation of silver in a colloidal form, and supports the view that the latent photographic image consists of colloidal silver in ultra-microscopic form (Lorenz and Hiege, Zeitsch. anorg. Chem. 1915, 92, 27).

It is also decomposed by intense light (Cordier, Monatsh. 1900, 21, 184; see also Baker, Chem. Soc. Trans. 1892, 728; Sonstadt, Chem. Soc. Proc. 1898, 371). Heated with calcium carbide, metallic silver is deposited (J. Soc. Chem. Ind. 1901, 1020). It also reacts with

iodoform giving chloroform and silver iodide (Coninck, Bull. Soc. chim. 1909, [iv.] 5, 62).

Digestion with potassium bromide or iodide solution decomposes the chloride with formation of potassium chloride and silver bromide or iodide (Field, Quart. J. Chem. Soc. 1858, 236). The chloride is converted into the bromide or iodide when fused in a current of air containing bromine or iodine vapour (Julius, Chem. News, 1853, 48, 284). It may be partly converted into the bromide by digestion with bromine water (*v.* Humpidge, Ber. 1884, 17, 1838; Potilizin, J. Russ. Phys. Chem. Soc. 1882, 82, and Ber. 1884, 17, 1309; Berthelot, Compt. rend. 1882, 94, 1619).

Silver chloride, bromide, or iodide, precipitated from solution containing a colouring matter such as an aniline dye, has a characteristic colour which cannot be removed by washing. The compounds produced by the different haloid salts with the same dye frequently differ considerably in colour. Somewhat similar compounds are obtained when silver chloride is precipitated from a solution containing a metallic salt, such as the chloride of iron, cobalt, nickel, manganese, copper, or gold (Carey Lea, J. Amer. Chem. Soc. 34, 384).

Dry precipitated silver chloride rapidly absorbs large volumes of ammonia gas, which it again gives off at 37.7° (Faraday, Quarterly J. of Sc. 5, 74). According to Rose (Pogg. Ann. 20, 157), the amount absorbed corresponds with the formula $2\text{AgCl}, 3\text{NH}_3$.

When a solution of silver chloride in liquid ammonia is allowed to evaporate at -40° to -20° , long colourless needles of the compound $\text{AgCl}, 3\text{NH}_3$ are deposited, but if a solution of silver chloride in concentrated ammonia is evaporated at ordinary temperature, the compound $2\text{AgCl}, 3\text{NH}_3$ separates in colourless prisms (Jarry, Compt. rend. 1897, 124, 288; Ann. Chim. 1899, [iv.] 17, 327; Biltz and Stollenwerk, Zeitsch. anorg. Chem. 1920, 114, 174).

For the action of an aqueous solution of sodium hyposulphite (hydrosulphite) on silver chloride, see J. B. Firth and J. Higson, J. Soc. Chem. Ind. 1923, 42, 427, T.

Colloidal silver chloride is obtained by the action of chlorine on colloidal silver or by treating the latter with chlorine water until the solution is decolorised, light being excluded during the process. To obtain a precipitate of the soluble chloride, gelatin and ammonium citrate are added (D. R. PP. 103406, 175794; Lottermoser, J. pr. Chem. [ii.] 56, 241; [ii.] 57, 540; *ibid.* 1905, [ii.] 72, 39; Paal and Voss, Ber. 1904, 37, 3862; Ruer, Chem. Zentr. 1905, i. 501; Drucker, Zeitsch. Chem. Ind. Kolloide, 1909, 4, 216).

Silver chloride formed a constituent of the sensitising material used in the original platinotype process (Willis, Photographic J. 1891, 123).

Silver bromide AgBr occurs native as *bromargyrite*. It is obtained by addition of a soluble bromide to silver nitrate, as a yellowish, curdy precipitate, less soluble in ammonia than the chloride, but more so than the iodide. It is also formed by the action of hydrogen bromide, and more slowly of bromine on metallic silver. Heat of formation 24,201 cal. In dilute ammonia it is almost insoluble. It dissolves in hot hydrobromic acid or mercuric nitrate

solution, and crystallises out in octahedra (*cf.* Marsh and Rhymes, *Chem. Soc. Trans.* 1913, 103, 785). It is also soluble in potassium and other bromides, forming double salts, and in sodium thiosulphate. According to Vogel (*Ber.* 1883, 16, 1170; 1885, 18, 861; *v.* also Eder, *ibid.* 18, 1256, and De Pitteurs, *Chem. Zentr.* 1884, 411), two molecular modifications of silver bromide exist, the one precipitated from aqueous solution, and the other from solution in alcohol of at least 96° p.c. The former is said to be most sensitive to certain of the blue rays, and the latter to certain of the indigo rays.

The solubility of silver bromide in water is found to be 0.107 mgrm. per litre at 21°, and 3.7 mgrms. at 100° (Kohlrausch and Dolezalek, *Sitzungsber. K. Akad. Wiss. Berlin*, 1901, 1018). It is more soluble in silver nitrate solution—three or four times more so than silver chloride, owing probably to the formation of $\text{AgNO}_3 \cdot \text{AgBr}$, which is known to exist.

Silver bromide fuses to a reddish liquid at 427° (Carnelley, *Chem. Soc. Trans.* 1878, 277). Its sp.gr., after fusion, is given by Schröder (*Pogg. Ann.* 106, 243) as 6.349, that of the precipitated bromide being 6.418. The electric conductivity of silver bromide is less than that of the chloride, but exceeds that of the iodide. When fused it conducts better than sulphuric acid.

Hydrogen chloride decomposes it at 700° with evolution of hydrogen bromide. Chlorine decomposes the freshly precipitated bromide.

According to Rammelsberg (*Pogg. Ann.* 55, 248), the dry bromide absorbs no ammonia; but it separates from ammoniacal solution in crystals containing ammonia, which is driven off by heat (Liebig, Schweigger's *J.* 48, 103).

Liquid ammonia below 4° converts silver bromide into a white compound $\text{AgBr} \cdot 3\text{NH}_3$, which loses ammonia at 4°, giving the compound $2\text{AgBr} \cdot 3\text{NH}_3$. The latter loses ammonia at 35°, leaving silver bromide (Jarry, *Compt. rend.* 1898, 126, 1138; Biltz and Stollenwerk, *Zeitsch. anorg. Chem.* 1920, 114, 174).

Colloidal silver bromide is obtained in the same way as the corresponding silver chloride.

Carey Lea describes peculiar compounds produced by precipitating silver bromide in presence of various colouring matters and metallic salts (*v. Silver chlorides*).

Regarding the sub- and photobromide, and the action of light on silver bromide, *v. Silver sub-salts*, &c.

Silver iodide AgI occurs naturally as *iodargyrite* or *iodyrite*. It may be obtained by heating silver with iodine, by dissolving silver in hydriodic acid, or by precipitating silver nitrate with a soluble iodide. Heat of formation 15,192 cal. (Krahmer, *Zeitsch. Elektrochem.* 1920, 26, 97); 14,990 cal. (Fischer, *Zeitsch. Elektrochem.* 1912, 18, 283); 15,000 cal. (Braune and Koreb, *ibid.* 1914, 87, 175); a number confirmed by Taylor and Anderson (*J. Amer. Chem. Soc.* 1921, 43, 2014); and by Gerth (*Zeitsch. Elektrochem.* 1921, 27, 287).

Silver iodide is of a pale primrose colour, and is insoluble in most acids, and almost insoluble in ammonia. Its solubility, however, increases appreciably with a rise in temperature. Its solubility in aqueous ammonia of sp.gr. 0.926 at 16° is 1 in 6000 (Baubigny, *Compt. rend.*

1908, 146, 263). It is slightly soluble in concentrated solutions of silver nitrate.

Silver iodide absorbs ammonia gas with formation of a white compound, of the composition $2\text{AgI} \cdot \text{NH}_3$, which evolves ammonia on exposure to the air (Rammelsberg, *Pogg. Ann.* 48, 170).

It is also readily soluble in liquid ammonia, and when the solution is evaporated at -40° to -10° , a white crystalline compound $\text{AgI} \cdot \text{NH}_3$ separates, which at 4° evolves ammonia, forming the compound $2\text{AgI} \cdot \text{NH}_3$ (Jarry, *Ann. Chim.* 1889, [vii.] 17, 327; Biltz and Stollenwerk, *Zeitsch. anorg. Chem.* 1920, 114, 174).

Silver iodide dissolves in potassium iodide and soluble thiosulphates; also in hot hydriodic acid, from which it separates on cooling in colourless flaky crystals of the composition $\text{AgI} \cdot \text{HI}$ (*v.* Deville, *Compt. rend.* 1851, 32, 894). It is decomposed by hot concentrated nitric or sulphuric acid with evolution of iodine. When gently heated in chlorine, or when heated to 700° in hydrogen chloride, it is converted into the chloride.

For the crystalline structure of silver iodide, *see* Wilsey (*Phil. Mag.* 1923, [vi.] 46, 487–496).

For the behaviour of silver iodide in the photo-voltaic cell, *see* Garrison (*J. Phys. Chem.* 28, p. 333, April, 1924; *Sci. Abstr.* 1924, 27, 773).

Crystalline double salts of silver iodide with the alkali-metal iodides have been described by Marsh and Rhymes (*Chem. Soc. Trans.* 1913, 103, 781). They are of the type $\text{MI}_2 \cdot 2\text{AgI}$ and $\text{MI}_3 \cdot 3\text{AgI}$. Lithium and silver iodides dissolve in acetone and yield hexagonal crystals of silver iodide.

When precipitated by excess of potassium iodide, silver iodide is unaffected by light, but it is rendered sensitive by the presence of a trace of silver nitrate, chloride, or bromide, which converts the last trace of potassium iodide into the silver salt (*v.* Abney, *Proc. Roy. Soc.* 33, 164).

The abnormal expansion and contraction of the iodide when heated was first noticed by Fizeau (*Compt. rend.* 1867, 64, 304), and has since been examined by Deville (*ibid.* 1867, 64, 323), Mallard and Le Chatelier (*ibid.* 1883, 97, 102), Bellati and Romanese (*Proc. Roy. Soc.* 34, 104), Rodwell (*ibid.* 33, 97; 25, 280; 31, 291), and Benedicks (*J. Iron and Steel Inst.* 1912, 86, 242). From -180° silver iodide has a positive coefficient of expansion which at -100° is 1.8×10^{-6} , but becomes imperceptible at 0° . From 40° to 140° gradual contraction occurs, followed by a sudden and very large contraction at about 147° . There is a much larger positive coefficient of expansion above 147° . With rapid heating the contraction from 140° onwards is more gradual and is only complete at 165° (*cf.* Jones and Hartmann, *J. Amer. Chem. Soc.* 1915, 37, 752). When heated it acquires a brilliant yellow colour and passes through various shades of orange, until, at 527° (Carnelley, *Chem. Soc. Trans.* 1878, 278; *see* also Stolzenberg and Huth, *Zeitsch. physikal. Chem.* 1910, 71, 641), it fuses to an orange-red liquid. On cooling the fused iodide, it contracts considerably at the solidifying-point, and continues to contract, until, at 116° , it expands suddenly, and passes from the amorphous to the crystalline form. The iodide appears to

exist in three modifications: (1) as a plastic, tenacious, amorphous, reddish, transparent substance between 116° and its melting-point; (2) as a brittle, opaque, crystalline mass below 116°; (3) as a yellow, brittle, amorphous mass, obtained by pouring the fused iodide into cold water.

The determinations of the specific gravity of the iodide vary considerably. According to Deville (Compt. rend. 1867, 64, 323), the sp.gr. of the fused iodide at 0° is 5·687, that of the precipitated iodide being 5·807 at 0°. According to Kohlrausch the electric conductivity of silver iodide is less than that of the bromide or iodide, but the conductivity of the fused salt exceeds that of sulphuric acid.

A saturated aqueous solution of silver iodide contains 0·0035 mgrm. per litre at 21° (Kohlrausch and Dolezalek, *l.c.*).

Colloidal silver iodide is obtained in the same way as the bromide and chloride, and also by the action of silver nitrate on potassium iodide dissolved in egg albumin (Thum, Amer. J. Pharm. 1910, 82, 507).

Carey Lea has described peculiar compounds produced by precipitating silver iodide in presence of various colouring matters and metallic salts (*v. Silver chlorides*).

Silver iodide, which may be separated from the chloride, with which it is often mixed, by digestion with ammonium carbonate and aqueous ammonia at 70°–80° (Baubigny, Compt. rend. 1908, 146, 335), was formerly employed in medicine, but it is now rarely used.

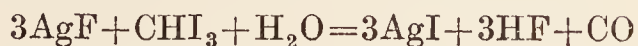
Regarding silver sub-iodide and photoiodides, *v. Silver sub-salts, &c.*

Silver fluoride $\text{AgF}_x\text{H}_2\text{O}$ may be obtained as a deliquescent, very soluble salt, by dissolving silver oxide in hydrofluoric acid. It crystallises from solution in quadratic pyramids, of the composition $\text{AgF}_x\text{H}_2\text{O}$ (Marignac, J. 1856, 129), or in prisms of the composition $\text{AgF}_x2\text{H}_2\text{O}$ (Frémy, J. 1856, 87; Pfaundler, J. 1862, 86); $\text{AgF}_x4\text{H}_2\text{O}$, m.p. 18·5° (A. and A. A. Guntz, Compt. rend. 1913, 157, 977). The formation of these hydrates is dependent on the temperature, the amount of hydrofluoric acid present, and is also a function of the nature of the saturated solution for a metastable or stable phase at the given temperature. Each of these hydrates dried in a vacuum over sulphuric acid yields amorphous silver fluoride. The hydrated salt loses water when dried *in vacuô*. Most of the water is driven off, together with some oxygen and hydrofluoric acid, when heated in a covered vessel to the melting-point of lead. After expulsion of all the water, the fluoride may be heated to the melting-point of silver without change. It can be obtained crystalline, in the form of ruby-red cubes, by evaporation *in vacuô*, of a solution of silver fluoride containing 5 p.c. of hydrofluoric acid. The dry salt absorbs 844 times its volume of ammonia. It forms an ammoniate of the composition: $\text{AgF}_x2\text{NH}_3, 2\text{H}_2\text{O}$ (Dervin and Olmer, Compt. rend. 1922, 175, 1058), crystallising in colourless orthorhombic prisms decomposed by light.

When a solution of the fluoride is strongly concentrated over the water-bath, or when the crystallised hydrated fluoride is dried over sulphuric acid, brass-yellow spangles, of the composition $\text{AgF} \cdot \text{AgHO}$, are obtained (Pfaundler, J.

1862, 87; *v. further*, Gore, Phil. Trans. 1869, 191, 192; 1870, 227; 1871, 321).

With aqueous iodoform it reacts thus:



(Coninck, Bull. Soc. chim. 1909, [iv.] 5, 62).

Silver fluoride has antiseptic properties, and under the name of *tachyol* has been proposed as an efficient and safe disinfectant for drinking waters (Paternò and Gingolani, Gazz. chim. ital. 1907, 37, i. 313).

Silver sub-fluoride *v. Silver sub-salts, &c.*

Silver chlorate AgClO_3 , formed by passing chlorine through silver oxide suspended in water or by dissolving silver in chloric acid, is a white, crystalline substance, m.p. 230°, which when mixed with sulphur detonates violently.

The perchlorate, hypochlorite, and chlorite are also known. Similar bromine compounds, a series of iodates and a number of the silver halogen double salts with the compounds of other metals have been prepared.

Silver bromate formed by double decomposition of silver nitrate and potassium bromate, is dimorphous, existing as tetragonal bi-pyramids (stable below 98·5°) and as hair-like crystals above this temperature. M.p. 308°–310°, stable towards light and heat, but darkens slowly in presence of water at the ordinary temperature and rapidly when heated. 100 grms. of water at 25° dissolve 0·196 gm., and at 90°, 1·325 grms. (Reedy, J. Amer. Chem. Soc. 1921, 43, 1440).

Silver iodate is a white crystalline powder, sparingly soluble in water. It is prepared by the action of silver nitrate on potassium iodate, and is employed in medicine externally and internally.

SILVER SUB-SALTS, PHOTOSALTS, AND SUB-OXIDE; ACTION OF LIGHT ON THE HALOID SALTS.

The existence of a suboxide of silver Ag_4O was first affirmed by Wöhler (Annalen, 1839, 30, 1), who stated that when silver citrate is heated to 100° in a current of hydrogen, it is reduced to a sub-citrate and free citric acid, 1 mol. of oxygen passing off as water. The residue dissolves in water to a brown solution, from which a black precipitate of the reputed suboxide is deposited on addition of potash. Wöhler's work was repeated by von Bibra (J. pr. Chem. 1875, [i.] 12, 39), Bailey and Fowler (Chem. Soc. Trans. 1887, 416), Newbury (Amer. Chem. J. 8, 196), and Muthmann (Ber. 1887, 20, 983). According to Bailey and Fowler, carbon dioxide is given off as well as water, except at the very earliest stages of the reduction, and the solution of the resultant body gives the reactions of itaconic acid and shows no argentous citrate. Newbury, however, while also noticing the evolution of carbon dioxide, and failing to obtain a sub-oxide, stated that the red solution is turbid from the presence of finely divided silver, and contains much free citric acid. Bailey and Fowler also failed to confirm Faraday's statement (Ann. Chim. [ii.] 9, 107), that a sub-oxide Ag_4O_3 is obtained by exposure of a solution of silver oxide in ammonia to the air.

O. v. der Pfordten (Ber. 1887, 20, 1458, 3375) obtained a black compound, which he

first described as the sub-oxide Ag_4O , but to which he subsequently gave the formula $\text{Ag}_4\text{H}_2\text{O}$ (*ibid.* 1888, 21, 2288), by the following process: 20 c.c. of a 12.5 p.c. solution of sodium tartrate was mixed with a solution of 2 grms. of silver nitrate in $1\frac{1}{2}$ litres of water, adding 2 c.c. of a 4 p.c. solution of soda, and stirring vigorously. After 5 hours the liquid was decanted, and the residual black precipitate of argentous tartrate (?) was washed with dilute sodium sulphate and treated with alkali, which converted it into the above compound. The same substance was obtained by the action of alkali on the black precipitate obtained by the gradual addition of 4 c.c. of concentrated phosphorous acid solution to a solution of 10 grms. of silver nitrate in 20 c.c. of water, to which sufficient ammonia had been added to re-dissolve the precipitate at first produced. The body thus obtained is a deep black amorphous powder, which is decomposed by water, and requires to be kept under alkali. It is insoluble in ammonia or acetic acid, and is decomposed, with separation of metal, by hydrochloric, sulphuric, and most other acids, but is not affected in the cold by sulphurous or phosphorous acid. Hydroxylamine has no action in the cold, but reduces it to silver when warmed; mercury fails to remove any silver. When acted on by sulphuretted hydrogen it produces black amorphous sulphide, which becomes grey when dried, and which is slowly decomposed by water. It dissolves in potassium cyanide and in warm dilute nitric and hydrochloric acids, water precipitating it unchanged from the latter. Strong nitric and sulphuric acids decompose it with separation of sulphur.

These results have been disputed by Bailey (*Chem. News*, 55, 263) and Friedheim (*Ber.* 1887, 20, 2554; 21, 307), the latter stating that the so-called argentous hydrate is a mixture of silver, with more or less argentic oxide and organic matter. See also Lewis (*J. Amer. Chem. Soc.* 1906, 28, 139). Geuther (*Annalen*, 114, 121) states that the sub-oxide is obtained by the action of precipitated cuprous oxide on silver nitrate; and, according to Guntz (*see below*), it is obtained by the action of steam on the sub-fluoride at 160° , but he gives no analysis of the product.

For the preparation of the sub-chloride, to which the formulæ Ag_2Cl (Wöhler) and Ag_4Cl_3 (von Bibra) have been applied, several methods have been proposed. Wöhler (*Annalen*, 1839, 30, 3) states that it is obtained as a black powder, which is decomposed by ammonia into silver chloride and silver by the action of hydrochloric acid on argentous citrate prepared as above. Wetzlar (*Schweigger's J.* 1828, 2, 466) states that it is produced by the action of cuprous or ferrous chloride on silver. Von Bibra (*J. pr. Chem.* 1875, [i.] 12, 39) and Newbury (*l.c.*) failed to obtain it by either Wöhler's or Wetzlar's process.

Guntz (*Compt. rend.* 1890, 110, 1337; 1891, 112, 861) prepared a fluoride of the composition Ag_2F by electrolysis of a saturated solution of the normal fluoride with a powerful current, using silver electrodes, and allowing the liquid to become hot. It is thus obtained on the cathode in brass-coloured plates, which are unaffected by dry air, but are rapidly decomposed by

water, with precipitation of silver and production of silver fluoride. The same compound is said to be produced when finely-divided silver is heated in a sealed tube, at a temperature below 90° , with silver fluoride solution. Compare Pfaundler (*Silver fluoride*). It may be obtained in large octahedral crystals which are quite stable when dry, even if exposed to light (Lothar Wöhler, *Zeitsch. anorg. Chem.* 1912, 78, 239).

According to Guntz the sub-fluoride is converted into the violet *sub-chloride* when dry hydrochloric acid, or, better, the vapour of the chloride of carbon, silicon, or phosphorus, is passed over it. Analysis of the sub-chloride indicates the presence of some normal chloride. Hydrogen iodide similarly gives a *sub-iodide* Ag_2I , with considerable rise of temperature. Sulphuretted hydrogen produces the *sub-sulphide* Ag_4S ; and steam passed over the sub-fluoride heated to 160° produces the sub-oxide.

Vogel has prepared the sub-halides according to the following method. Cupric bromide (or other halide) was boiled with copper shavings, and the green solution poured into 10 times the quantity of water and boiled with acetic acid. The white powder so obtained is dried quickly and treated at once with excess of 10 p.c. silver nitrate solution, a blackish-grey *sub-bromide* Ag_4Br_2 is thus obtained, which may be freed from copper by repeated digestion with 20 p.c. silver nitrate solution (*J. Soc. Chem. Ind.* 1900, 374; Waterhouse, *ibid.* 374).

According to Emszt (*Zeitsch. anorg. Chem.* 28, 346) Vogel's sub-haloids are not identical with those formed by the action of light on photographic plates.

Carey Lea (*Amer. J. Sci.* 33, 349, 480, 489; 34, 33) has produced an important series of coloured haloid salts of silver, to which he has given the name 'photosalts,' and which he regards as identical with the so-called sub-salts forming the latent photographic image. They appear to be compounds of the normal and sub-salts, the proportion of halogen in the chlorides corresponding to from under 1 p.c. to over 8 p.c. of the sub-chloride; in the iodide, corresponding to from 0.64 to 4.63 p.c.; and in the bromide sometimes corresponding to as much as 7 p.c. of the sub-salt.

For the photochemical decomposition of silver chloride, *see* Schwarz and Gross (*Zeitsch. anorg. Chem.* 1924, 133, 389; *Chem. Soc. Abstr.* 1924, 126, ii. 550).

The photochloride, which the bromine and iodine compounds resemble in general properties and methods of preparation, may be obtained in various colours, varying through salmon, pale pink, rose, copper-red, reddish purple, chocolate, and other shades, to black.

The following are some of the methods of preparation: (1) the chlorination of the metal, best by the action of a freshly prepared chlorine solution on freshly prepared colloidal silver, the salt in this case being of a rose-red colour; (2) the partial reduction of the normal chloride; (3) the reduction of silver oxide or carbonate by heat, with subsequent treatment by hydrochloric acid; (4) the treatment of the sub-oxide or a sub-salt with hydrochloric acid, followed by nitric acid; (5) the treatment of the sub-chloride with nitric acid or an alkaline hypochlorite; (6) the treatment of a solution of

silver nitrate with ferrous, manganous, or chromous oxide, and treatment of the product with hydrochloric acid; (7) the treatment by hydrochloric acid of the product of the reduction of silver citrate in hydrogen; (8) treatment of a silver solution with potash or soda and a reducing agent, such as milk sugar, or any easily oxidisable body, the precipitate being treated with hydrochloric acid.

The photosalts are formed when the halogen salts of silver are allowed to remain in contact or are warmed with colloidal solutions of silver, the excess of silver being subsequently removed by solution in nitric acid. They are also obtained by adding a suitable reducing agent to silver nitrate, which is in contact with an ordinary silver halogen salt. The reducing agents recommended are (1) sodium citrate or potassium tartrate and ferrous sulphate; (2) tannic or gallic acid and alkali carbonate; (3) formaldehyde and sodium hydroxide; (4) sodium hypophosphite (Lüppo-Cramer, *Zeitsch. Chem. Ind. Kolloide*, 1907, 2, 135; *ibid.* 1908, 2, 360; *ibid.* 3, 33, 135).

Reinders (*Chem. Weekblad*. 1910, 7, 961; 1911, 8, 299) has prepared crystalline photochloride of silver by crystallising silver chloride from dilute aqueous solutions of ammonia in presence of sunlight. The crystals have an indigo-blue colour, the depth of tint depending on the intensity of the light and the duration of crystallisation. The darkest crystals contained 1 p.c. of free colloidal silver. The colour of the crystals undergoes various changes on exposure to light or to variously coloured glass.

These salts are permanent in the dark, but become purple or purplish-black when exposed to light. They are all decomposed by strong nitric acid, and slowly dissolve in ammonia, ammonium chloride, or sodium chloride, leaving a little silver. When heated, the photosalts are altered in colour, usually towards redness. Thus the grey salt may become pink at 100°, while the dark varieties may turn chocolate-colour or purple at that temperature.

Hydrogen peroxide also induces a series of colour changes in the photohalides from green to blue, then to red. The green salt contains most silver, and is least sensitive to light, whilst the red contains most silver and is most sensitive (Trivelli, *Chem. Zeit.* 1909, 33, 844; *Chem. Weekblad*. 1910, 7, 351; *ibid.* 404).

The action of light on the chloride, which seems to have been first noticed by Conrad Gessner in 1565, in the case of horn silver, and similarly on the bromide and iodide, has been variously attributed to the production of metal, sub-chloride and oxy-chloride; and to the formation of a photochloride.

The evolution of chlorine under the action of light is indisputable, but the composition of the residue is still doubtful. Some chemists consider it to be a mixture of the normal chloride and silver, whilst others consider that the product in the case of silver bromide consists of the unchanged salt with a sub-bromide and metallic silver. Basing his conclusions on measurements of solubility of electrical potential, Sichling (*Zeitsch. physikal. Chem.* 1911, 771) considers the photochlorides to be solid solutions of silver chloride and amorphous silver, the half chloride Ag_2Cl is probably also present, but is of little

importance in the system (Carey Lea, *l.c.*; Staats, *Ber.* 1887, 20, 2322; 1888, 21, 2199; Newbury, *Amer. Chem. J.* 6, 407; Tommasi, *Bull. Soc. chim.* [ii.] 37, 291; Abney, *Proc. Roy. Soc.* 33, 164; *ibid.* 40, 251; Griveaux, *Compt. rend.* 1888, 107, 837; Richardson, *Chem. Soc. Trans.* 1891, 536; *Chem. Soc. Proc.* 1898, 179; Eder, *Chem. Zeit. Rep.* 1899, 196; Abegg, *Chem. Zentr.* 1899, i. 649; *J. Soc. Chem. Ind.* 1900, 70; Baur, *Zeitsch. physikal. Chem.* 1904, 45, 613; Trivelli, *Zeitsch. wiss. Photograph. Photophysik. und Photochem.* 1908, 6, 358; *Proc. K. Akad. Wetensch. Amsterdam*, 1909, 11, 730; Lüppo-Kramer, *l.c.*; Lorenz and Hiege, *Zeitsch. anorg. Chem.* 1915, 92, 27). According to Hartung (*Chem. Soc. Trans.* 1922, 121, 682) silver bromide loses 2.5 p.c. of its bromine when exposed to light in air; *in vacuô* it loses 80 p.c. of its bromine, and the loss is still greater by long exposure to light in an atmosphere of nitrogen. Light appears to cause the formation of a solid solution (presumably colloidal) of metallic silver in the halide salt; there is no certain evidence of the formation of a sub-halide, or of an oxy-halogen. Ehlers and Koch (*Zeitsch. Physikal. Chem.* 1920, 3, 169) found that a particle of silver bromide 3×10^{-12} grm. loses on illumination for 20 minutes by an arc lamp 6 p.c. of its weight of bromine. Comparative experiments with a specially rapid silver bromide gelatin plate showed that the bromine particle when illuminated for 1/100 sec. by a light intensity 1/10000 of that used in the foregoing experiment loses 1.5×10^{-22} gram of bromine, that is approximately one atom per particle (*cf.* Schwarz and Stock, *Ber.* 1921, 54, B, 2111); *see also article on PHOTOGRAPHY*).

The increased sensitiveness of silver bromide to light when mixed with silver iodide is held to be due to a weakening of the bond between silver and bromine, which is of the nature of an increase in the distance between the two atoms. This brings the molecule into such a condition that less energy is required to liberate an atom of bromine than is necessary with pure silver bromide (A. P. H. Trivelli, *Rec. trav. chim.* 1923, 42, 714-717; *J. Soc. Chem. Ind.* 1923, 42, 908, A.).

Attempts have been made to find the relationship between the age and the photochemical decomposition of silver bromide, using the mercury lamp as a source of light. Very irregular curves were, however, obtained, the irregularities being ascribed to moisture, the loss of which decreased the rate of separation of bromine, and to grain size, which increased with age. Colloidal sols act as catalysts, silica being positive, and platinum, zirconium hydroxide, stannic acid, and gelatin negative catalysts (R. Schwarz and H. Stock, *Zeitsch. anorg. Chem.* 1923, 129, 41-54; *J. Soc. Chem. Ind.* 1923, 42, 1248, A.).

For the spectral sensitiveness of silver bromide and the influence of absorbed substances on the sensitiveness, *see* W. Frankenburg (*Zeitsch. physikal. Chem.* 1923, 105, 273-328; *J. Chem. Soc.* 1923, 123, 124, ii. 599).

For the conditions which determine the photosensitiveness of silver iodide, *see* Germann and Hylan (*J. Amer. Chem. Soc.* 1923, 45, 2486; *Chem. Soc. Abstr.* 1924, 126).

Hitchcock (Amer. Chem. J. 11, 474) found as much as 4.2–4.9 p.c. of chlorine eliminated from thin films of silver chloride exposed to sunlight in a *current of hydrogen*. Carey Lea (Amer. J. Sci. 38, 356) has shown that anhydrous silver chloride or iodide is darkened by light under petroleum, where the production of any quantity of oxychloride is impossible. Richardson has made a similar experiment with carbon tetrachloride (Chem. Soc. Trans. 1891, 544).

Regarding the action of dyes in modifying the sensitiveness of silver to different parts of the spectrum (orthochromatic photography) *v.* Vogel (Ber. 1873, 6, 1302); Eder (Sitz. Ber. 1884, 1117; Monatsh. 6, 1; 7, 1); Bothamley (J. Soc. Chem. Ind. 1887, 423; Brit. J. of Photography, 35, 499); Valenta (J. Soc. Chem. Ind. 1900, 375); Günther (*ibid.* 1905, 1083); Mees and Wrathall (Phot. J. 1906, 46, 300; D. R. P. 376051); *see also* PHOTOGRAPHY.

ORGANIC SALTS OF SILVER.

A number of organic salts of silver are employed in medicine as substitutes for silver nitrate, which is open to the objection of combining with the albumin and the sodium chloride of the tissue fluids forming an insoluble compound, and thus losing in penetrative power. These compounds possess great penetrability, are not precipitated by saline and albuminous solutions, and their aqueous solutions are generally not decomposed by weak acids, alkalis, alkali sulphides, or sodium chloride.

Silver citrate (*Itrol*) $\text{Ag}_3\text{C}_6\text{H}_5\text{O}_7$ is a white, odourless, heavy powder, obtained by precipitating a solution of silver nitrate with a solution of citric acid neutralised with sodium bicarbonate.

Silver lactate (*Actol*) $\text{AgC}_3\text{H}_5\text{O}_3 \cdot \text{H}_2\text{O}$ is obtained by dissolving silver carbonate in dilute lactic acid in the dark. It forms colourless needles, which turn brown rapidly on exposure to light.

Silver acetate, $\text{AgC}_2\text{H}_3\text{O}_2$, prepared by the action of sodium acetate on silver nitrate, forms white, minute crystals of a disagreeable metallic taste.

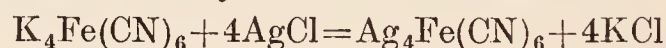
Silver tartrate $\text{Ag}_2\text{C}_4\text{H}_4\text{O}_6$ is obtained as a white curdy precipitate on mixing solutions of Rochelle salt and silver nitrate. It is nearly insoluble in water, but dissolves in dilute ammonia. This solution deposits its silver as a shining mirror when gently heated, and under various modifications, and is largely employed in silvering glass. A good mixture is prepared as follows: (1) Dissolve 5 grms. of silver nitrate in 100 c.c. of distilled water and add ammonia until the precipitate first produced is nearly dissolved. (2) Dissolve 1 gram. of silver nitrate in 20 c.c. of water, heat to 43° , and add a solution of 0.83 gram. of Rochelle salt in 10 c.c. of water. Boil the mixture for 10 mins., filter, and dilute to 500 c.c. The glass, after washing with potash, dilute nitric acid, and alcohol, rinsing after the application of each, is covered with a mixture of equal volumes of these solutions at about 27° . After an hour the silver will have deposited in a coherent film, which may be polished or varnished after a few days (*v.* Cooley's Cyc. of Practical Receipts, 1872, 1044; Varley, Year-book of Photography, 1890, 114).

For an account of the various factors involved in the deposition of mirror silver by reducing an ammoniacal solution of silver hydroxide, *see* Kohlschütter and Fischmann, Annalen, 1912, 387, 86; J. Soc. Chem. Ind. 1912, 31, 188).

W. H. Perkin (Chem. Soc. Trans. 1887, 362) describes an acid tartrate $\text{C}_4\text{H}_5\text{AgO}_6 \cdot \text{H}_2\text{O}$ crystallising in large brilliant monoclinic prisms, from a mixture of strong silver nitrate and tartaric acid solutions.

Silver fumarate $\text{C}_4\text{H}_2\text{Ag}_2\text{O}_4$ is precipitated as a white amorphous powder, requiring over 200,000 parts of water for solution, by addition of the acid or its salts to a solution of silver nitrate. It explodes on heating. Warnerke (Year-book of Photography, 1876, 131) has proposed its use in photography.

Silver ferrocyanide $\text{Ag}_4\text{Fe}(\text{CN})_6$ is a white insoluble compound formed by the action of potassium ferrocyanide on silver chloride:



Nitric acid converts it into the orange-red silver ferricyanide. This reaction may be employed to detect the presence of silver chloride on photographic plates, films, &c. For details, *see* Valenta (Chem. Zeit. 1916, 40, 398).

The crystalline double compound of silver **succinimide** and **hexamethylenetetramine** is obtained by dissolving the constituents in water, aqueous methyl, or ethyl alcohol or aqueous acetone, and warming the solutions *in vacuo* until crystallisation commences. The concentrated solutions of this compound are stable, are not discoloured by light, and do not coagulate albumin (D. R. P. 217897). Other silver double salts with hexamethylenetetramine, employed in medicine, have been prepared (D. R. PP. 193740, 213712, 209340).

Argentamine (*Ethylene-diamine silver phosphate*) is made by dissolving 10 parts of silver phosphate and 10 of ethylenediamine in 100 of water. It forms a colourless alkaline solution not precipitated by chlorides or by albumin. Similar compounds are described in Fr. Pat. 400627, 1909.

When silver nitrate reacts with tetraethylammonium iodide a compound $(\text{C}_2\text{H}_5)_4\text{NI} \cdot 2\text{AgI}$ is formed. The substance is pure white, quite stable to light, and melts with very slight decomposition at 225° – 230° to a light yellow liquid (Strömholm, Ber. 1903, 36, 142).

Silver phenol sulphonate $\text{C}_6\text{H}_4(\text{OH})\text{SO}_3\text{Ag}$ is obtained by dissolving silver carbonate in *p*-phenolsulphonic acid, and evaporating to crystallisation in the dark. It forms colourless, odourless, prismatic crystals, decomposed by light, and when heated at 120° . It is soluble in aqueous alcohol, has a metallic taste, is antiseptic and non-corrosive, and, like itnol and argonin, is employed in eye diseases and for wounds (Zanardi, Chem. Zentr. 1898, ii. 712).

Argentol (*silver quin-aseptolate, silver oxy-quinoline sulphonate*) $\text{C}_9\text{H}_5\text{N}(\text{OH})\text{SO}_3\text{Ag}$ is a yellow powder sparingly soluble in water, alcohol, or in ether, more so in hot water. It is formed by the interaction of silver nitrate and sodium quinaseptolate. It is employed in medicine as a substitute for iodoform.

Argonin is a compound of silver and casein

containing about 4 p.c. of the metal. It is prepared by adding silver nitrate solution to the sodium salt of casein and precipitating with alcohol.

Argyrol is a proteid salt of silver containing 30 p.c. of silver. It dissolves readily in water, forming stable solutions. It is employed for a variety of purposes in medicine, even strong solutions producing no pain or irritation (Nat. Stand. Dispensatory, 1905, 238).

Nargol is a compound of silver (10 p.c.) with nucleic acid derived from yeast. It is readily soluble in water and is used in the treatment of gonorrhœa, and in inflammation of the conjunctiva.

A soluble double compound of paranuclein and a silver salt is formed by adding the latter to an alkaline solution of paranuclein. Acid is added and the precipitate formed is dissolved in sodium hydroxide solution and then separated by evaporation (Eng. Pat. 4507, 1901).

Soluble silver nucleic acid compounds, having antiseptic properties, are formed by treating salts of nucleic acids with silver nitrate. The precipitate so formed is re-dissolved by the addition of a neutral salt such as sodium chloride, and the silver nucleic acid compound is isolated by precipitation with alcohol or evaporation *in vacuo* (Eng. Pat. 8407, 1906).

Protargol is a compound of protein and silver; it is a yellow powder with a weak metallic taste, soluble in water, and is said to be an excellent non-irritant bactericide.

Largin is a silver albumin compound containing 11.1 p.c. silver.

For the properties of silver organosols, *v.* Giles and Salmon (Chem. Soc. Trans. 1923, 123, 1597).

Silver also forms salts with acetylene (Maguire, J. Amer. Chem. Soc. 1906, 28, 1025; Mees and Wrattan, Phot. J. 1908, 48, 338).

If acetylene gas is led into a solution of silver nitrate acidified with nitric acid, a white precipitate is formed, which can be dried safely at 100°, is insensible to friction or percussion, but explodes violently when heated. If potassium chlorate is added to the silver nitrate, the substance formed is also sensible to friction (Fr. Pat. 321385, 1902).

For other organic compounds of silver, *see* Eng. Pats. 26353, 1901; 23507, 1902; Fr. Pat. 380197, 1907; D. R. P. 218728; Charabot and March, Bull. Soc. chim. 1899, [iii.] 21, 552; Liebermann, Ber. 1902, 35, 1094; Kahlenberg, J. Phys. Chem. 1908, 12, 283; *ibid.* 1909, 13, 421; J. Chem. Ind. 1909, 707; Lüppe-Cramer, Zeitsch. Chem. Ind. Kolloide, 1908, 2, 325; Doughty, J. Amer. Chem. Soc. 1909, 41, 326; Angelli, Atti R. Accad. Lincei, 1909, [v.] 18, ii. 38; *ibid.* 1910, [v.] 19, i. 784.

SILVER ARSPENAMINE. The sodium salt of silver diamino-dihydroxy-arsenobenzene (silver-salvarsan). A brownish-black powder, unstable in air, readily soluble in water, forming a dark-brown solution with an alkaline reaction. May be distinguished from arsenobenzol by the colour and alkalinity of its solution. Gives no precipitate with dilute sodium hydroxide, or sodium carbonate solutions. Used in the treatment of syphilis and other spirochætal infections

and in protozoal diseases such as malaria and trypanosomiasis.

SILVER ASSAYING *v.* ASSAYING.

SILVERING is the art of covering the surface of bodies with a thin film of silver. This is now effected either by applying thin films of silver mechanically to the article to be silvered, or by the electro-metallurgical process. When silver leaf is to be applied, the methods prescribed for gold leaf are suitable. Among the metals, copper or brass are those on which the silverer most commonly operates. Iron is seldom silvered, but the process for both metals is essentially the same. The white alloy of nickel is now often plated.

The principal steps of this operation are the following:—

1. The *smoothing down* the sharp edges, and polishing the surface of the copper; called *émorfiler* by the French artists.

2. The *annealing*; or making the pieces to be silvered red hot, and then plunging them in a very dilute nitric acid till they are bright and clean.

3. *Pumicing*; or clearing up the surface with pumice-stone and water.

4. The *warming*, to such a degree merely as when it touches water it may make a slight hissing sound; in which state it is dipped in very weak aquafortis, whereby it acquires minute insensible asperities, sufficient to retain the silver leaves that are to be applied.

5. The *hatching*.—When these small asperities are inadequate for giving due solidity to the silvering, the plane surfaces must be hatched all over with a graving tool, but the chased surfaces need not be touched.

6. The *blueing* consists in heating the piece till its copper or brass colour changes to blue. In heating they are placed in hot tools made of iron, called *mandrins* in France.

7. The *charging*; the workman's term for silvering. This operation consists in placing the silver leaves on the heated piece, and fixing them to its surface by burnishers of steel of various forms. The workman begins by applying the leaves double. Should any part darken in the heating, it must be cleared up by the scratch-brush.

The silverer always works two pieces at once, so that he may heat the one while burnishing the other. After applying two silver leaves he must heat up the piece to the same degree as at first, and he then fixes on with the burnisher four additional leaves of silver, and he goes on charging in the same way, four or six leaves at a time, till he has applied, one over another, 30, 40, 50, or 60 leaves, according to the desired solidity of the silvering. He then burnishes down with great pressure and address till he has given the surface a uniform silvery aspect. A French patent (366785, 1906) describes a special process of preparing the silver leaf used in these operations.

Silvering by the precipitated silver chloride. The white curd, obtained by adding a solution of common salt to one of silver nitrate, is to be well washed and dried. 1 part of this powder is to be mixed with 3 parts of good pearlash, 1 of washed whiting, and 1½ of sea salt; or 50 parts of the chloride are mixed with 150 of potassium cyanide, 15 of aluminium nitrate,

50 thorium nitrate, 100 potassium bitartrate, 300 distilled water, and 350 of chalk (Fr. Pat. 320154, 1902). After cleaning the surface of the brass it is to be rubbed with a piece of soft leather, or cork moistened with water and dipped in the above powder. After the silvering it should be thoroughly washed with water, dried, and immediately varnished. Some use a mixture of 1 part of the silver precipitate with 10 of cream of tartar, and this mixture also answers very well.

Others give a coating of silver by applying with friction, in the moistened state, a mixture of 1 part of silver powder precipitated by copper, 2 parts of cream of tartar, and as much common salt. The piece must be immediately washed in tepid water very faintly alkalisied, then in slightly warm pure water, and finally wiped dry before the fire.

Various other mixtures are employed thus: the silver chloride may be dissolved in aqueous sodium thiosulphate and the solution mixed with 8 p.c. ammonium chloride solution, ammonia and levigated chalk (Fr. Pat. 355518, 1905). A mixture of the chlorides of silver and iron, or copper, together with those of the alkaline earths or of magnesium or aluminium has been employed (D. R. P. 118922).

Another process consists in the use of silver resinate. The latter is obtained by the interaction of an alkali resinate and a soluble silver salt in aqueous solution or by heating resin with an easily decomposable silver salt or with silver oxide. The silver resinate is dissolved in benzene and the solution is applied to the surface to be coated. The benzene is allowed to evaporate in the dark, and the article is then either exposed to the light for some time or treated with a solution of hydroquinone or pyrogallol in ethyl or methyl alcohol. The resin is then removed from the reduced silver by means of a suitable solvent. This process may also be used for plating the interior surface of articles (Fr. Pat. 380886, 1906).

The inferior kinds of plated buttons get their silvery coating in the following way:—

Two ozs. of silver chloride are mixed with 1 oz. of corrosive sublimate, 3 lbs. of common salt, and 3 lbs. of zinc sulphate with water into a paste. The buttons, being cleaned, are smeared over with this mixture and exposed to a moderate degree of heat, which is eventually raised nearly to redness, so as to expel the mercury from the amalgam formed by the reaction of the horn silver and the corrosive sublimate. The copper button thus acquires a silvery surface, which is brightened by cleaning and burnishing.

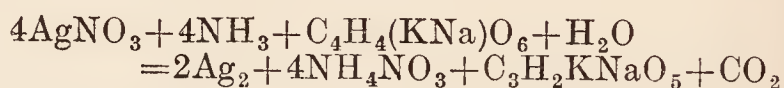
A mixture for silver plating, whereby cleaning, scouring, and plating are said to be carried out in one process, consists of: 15 parts of silver nitrate converted into silver chloride by hydrochloric acid, 350–400 of tripoli powder or jeweller's rouge, or fine emery, 80–100 of acetic acid or vinegar, 300–350 sodium chloride or sodium nitrate, and 1 litre water (Eng. Pats. 14324, 6589, 1899), the unprepared article being rubbed with the mixture.

To produce a coating of silver on paper or leather, a mixture of ammonium silver nitrate and of a reducing salt (prepared by boiling aqueous potassium sodium tartrate with sugar)

is applied to a glass plate, and the silver film formed is washed, dried, and covered with a warm solution of gelatin. The paper or leather to be coated is now laid on the film and rolled. After drying the film is stripped from the glass surface and adheres to the paper or leather (Eng. Pat. 20709, 1903; see also Eng. Pat. 4385, 1908).

To render the silver surface non-tarnishable the article is sometimes coated with a layer of zinc or other metal which will alloy with silver, but will not combine with sulphur. The article is then subjected to pressure by placing it in a closed cylinder into which a liquid such as petroleum or a solution of a salt of the coating metal is pumped (Eng. Pats. 25966, 1906; 16538, 16539, 18210, 1907; J. Soc. Chem. Ind. 1908, 947). Silver mirrors are sometimes protected with a film of celluloid (Perot, Compt. rend. 1909, 149, 725).

The silvering of glass for the manufacture of mirrors is carried out by a variety of processes, in most of which ammoniacal silver nitrate and some reducing agent are employed, but each worker seems to have his own recipe. The tartrates, however, give the most brilliant surfaces. The substances should be taken approximately in the proportions expressed by the following equation:



but the tartrate should be in slight excess.

A portion of the silver nitrate solution is mixed with the tartrate, warmed and filtered after the liquid has blackened. Ammonia is then added to the rest of the silver nitrate until the precipitate first formed is redissolved. The mixture of the two solutions deposits silver easily and uniformly. Before the deposition of the silver the glass surface should be prepared by washing with stannous chloride and rinsing with water.

For the conditions determining the production of mirror silver, see Kohlschütter and Fischmann, *Annalen*, 1912, 387, 86.

For the silvering of glass by the formol process, see Cotton (Rev. d'Optique, 1924, 3, 57; Sci. Abstr. 1924, 27, 579).

The nature of the varnish employed to protect the film is also of great importance, as many substances are liable to attack the thin silver coating. Shellac is usually employed, but a mixture of resin with an insoluble base, such as zinc or magnesia, is said to be very good (Fafet, Rev. Chim. Ind. 1898, 9, 5). A process of silvering mirrors in which formaldehyde, together with glycerin, gum or sugar solution are used, is described in a Fr. Pat. (392243, 1908; J. Soc. Chem. Ind. 1908, 1204); see also Silverman and Howe, J. Ind. and Eng. Chem. 1917, 9, 1032 (v. art. on ELECTROPLATING).

For an account of the silver industry of Sheffield, see Ernest Smith, J. Soc. Chem. Ind. 1911, 30, 997.

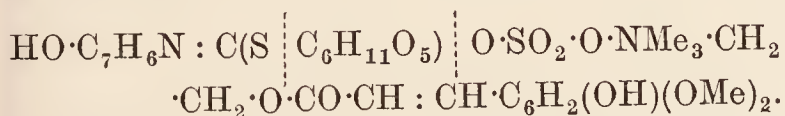
SILVER SALT. A factory term for sodium anthraquinone-2-sulphonate.

SILVER WHITE. *Blanc d'argent* v. PIGMENTS.

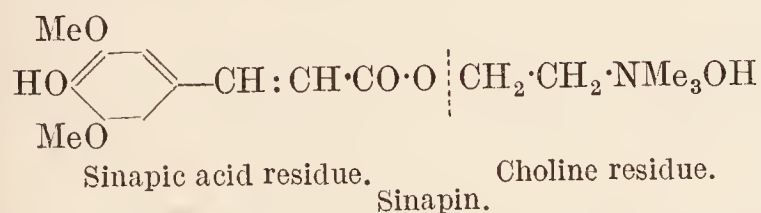
SIMILOR. A rich-coloured brass, said to be composed of 3 ozs. of zinc to 1 lb. of copper.

SINALBIN $\text{C}_{30}\text{H}_{42}\text{O}_{15}\text{N}_2\text{S}_2$, first isolated by

Will and Laubenheimer from white mustard seed (Annalen, 1879, 199, 162). Crystallises with $5\text{H}_2\text{O}$, m.p. $83^\circ\text{--}84^\circ$; anhydrous, m.p. 139° . Lævo-rotatory (Gadamer, Apoth. Zeit. 1896, 11, 752; Arch. Pharm. 1897, 235, 44, 570). Sinalbin is one of a series of closely related glucosides from plants belonging to the *Crucifera*, e.g. sinigrin (potassium myronate), gluconasturtiin, and glucotropæolin, all of which on hydrolysis by enzymes furnish dextrose, a mustard oil (alkylthiocarbimide) and a third substance. In the case of sinalbin the third substance is *Sinapin* (see below), whilst in the three other glucosides mentioned it is potassium hydrogen sulphate. According to Gadamer (*l.c.*) sinalbin is hydrolysed into *p*-hydroxybenzylthiocarbimide, dextrose, and sinapin hydrogen sulphate, and has the following constitution, in which the dotted lines show the residues of the three components:



SINAPIN $\text{C}_{16}\text{H}_{25}\text{O}_6\text{N}$ occurs in white mustard seed from which it may be isolated by extraction with alcohol and precipitation as the thiocyanate, m.p. 176° , which is stable, though sinapin itself is so unstable that it cannot be kept in the free state. It is an ester of choline and sinapic acid, and, according to Gadamer, has the following constitution—

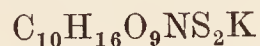


Späth (Monatsh. Chem. 1920, 41, 271) has prepared sinapic acid synthetically and converted it into sinapin iodide, which has the constitution proposed by Gadamer for the product derived from the natural sinapin. The acid sulphate $\text{B}\cdot\text{H}_2\text{SO}_4\cdot 3\text{H}_2\text{O}$ forms rectangular leaflets, m.p. 127° . The chief papers relating to sinapin are: von Babo and Hirschmann, Annalen, 1852, 84, 10; Will and Laubenheimer, *ibid.* 1879, 199, 162; Remsen and Cole, J. Amer. Chem. 1884, 6, 52; and Gadamer, Arch. Pharm. 1897, 235, 44, 570; Apoth. Zeit. 1896, 11, 572).

SINAPOLINE. *Diallyl-urea* $\text{CO}(\text{NH}\cdot\text{C}_3\text{H}_5)_2$. A crystalline substance obtained by boiling mustard oil with baryta water or lead oxide.

SINIGRIN. A glucoside found in black mustard, easily soluble in water, slightly soluble in 96 p.c. alcohol, insoluble in amyl and isobutyl alcohols, ether, acetone, or chloroform, somewhat soluble in warm methyl alcohol, melts and becomes brown at 130° , gives a white precipitate with basic lead acetate in presence of ammonia, a yellowish-red coloration, but no evolution of mustard oil when boiled with 33 p.c. solution of potassium hydroxide. Hydrolysed by myrosin, but by no other hydrolytic enzyme, with formation of allyl isothiocyanate (Gonnermann, Pflüg. Arch. Phys. 1911, 137, 453; J. Soc. Chem. Ind. 1911, 30, 305). Thioglucose obtained from sinigrin is not identical with that prepared

synthetically, as shown by the fact that it is lævo-rotatory, while that prepared synthetically is dextro-rotatory, and by the comparison of the penta-acetyl derivatives. It is suggested that the two compounds are the α and β forms, which are presumably more stable than the corresponding forms of dextrose. Sinigrin has been obtained in an anhydrous form



compact, white, glistening needles, m.p. 79°C ., $[\alpha]_D = -16.13^\circ$ in water. This indicates that the decomposition of sinigrin by the enzyme myrosin is a simple hydrolysis:



(F. Wrede, E. Banik, O. Brauss, Zeitsch. physiol. Chem. 1923, 126, 210; J. Soc. Chem. Ind. 1923, 516, A.) For constitution, see Schneide and Wrede, Ber. 1914, 47, 2225.

SINODOR. A term for a basic magnesium acetate (*v.* ACETIC ACID; also MAGNESIUM).

SINTER. A name applied to incrustations on rocks or elsewhere, from mineral waters. According to the nature of the deposit, it is distinguished as calcareous sinter (travertine), siliceous (quartz or opal), ferruginous (pitticite), arsenical (scorodite), &c.

SIOMINE. Hexamethylenetetraminetetraiodide.

SIPYLITE. Columbate of erbium (Er_2O_3 27, Y_2O_3 1 p.c.) and cerium earths (Ce_2O_3 , &c., 9 p.c.) crystallised in the tetragonal system. Crystals, which are pyramidal in habit, are rare, the mineral being usually found as irregular masses with a brown colour and resinous lustre. Sp.gr. 4.89. It occurs with orthite and magnetite at Little Friar Mountain in Amherst Co., Virginia.
L. J. S.

SISSERSKITE, SYSERTSKITE *v.* IRIDOSMINE.

SIUM LATIFOLIUM OIL. The crushed seeds of the umbelliferous plant, *Sium latifolium*, L., yield about 6 p.c. of an essential oil similar to oil of caraway in character, consisting, like the latter, of two main constituents. The lower-boiling constituent, present to the extent of 80 p.c., is *d*-limonene, whilst the higher-boiling fraction gives an oxime, m.p. $101^\circ\text{--}102^\circ$, $[\alpha]_D = +136.76^\circ$, derived from a ketone not identical with carvone. The physical characters of the oil are sp.gr. at 25.5° 0.8533, $[\alpha]_C = 177.24^\circ$, $[\alpha]_D = +98.40^\circ$, $[\alpha]_E = +127.24^\circ$, $[\alpha]_F = 153.80^\circ$ (G. V. Pigulevski, J. Russ. Phys. Chem. Soc. 1922, 54, 296–303; J. Soc. Chem. Ind. Sept. 7th, 1923, 859, A).

SKIMMIA LAURCOLA. The leaves of this plant contain an essential oil, pale emerald-green in colour. D_{30}^{30} 0.9041, n_D^{30} 1.4648, acid value 3.63, saponification value 197.96, saponification value after acetylation 238.6. The oil consists mainly of *l*-linalyl acetate, and contains in addition *l*-linalool, sesquiterpene alcohols and esters, together with a hydrocarbon, b.p. $130^\circ\text{--}135^\circ/200$ mm., $176^\circ\text{--}182^\circ/695$ mm. D_{30}^{30} 0.859, n_D^{30} 1.471, $[\alpha]_D^{30} = -4.11^\circ$ (Simonsen, J. Soc. Chem.

Ind. 1921, 40, 126). Cf. Roure-Bertrand, Fils. Sci. Ind. Bull. 1920, [iv.] No. 2, 29, whose numbers are markedly different.

SKIMMIN *v.* GLUCOSIDES.

SKUTTERUDITE. *Cobalt triarsenide v. COBALT.*

SLAG, BASIC, v. FERTILISERS.

SLATE. (*Ardoise, Schiste ardoise, Fr.; Thonschiefer, Ger.*) A fine-grained sedimentary rock, usually argillaceous, characterised by a highly fissile structure. The fissility, termed *slaty cleavage*, is due to a rearrangement of the particles of the rock consequent on compression, and it has been shown by Sorby and others that the direction of cleavage is at right angles to that in which the earth pressure was applied; hence the planes of cleavage need not bear any relation to the original bedding of the rock. (For an able discussion of the subject of slaty cleavage, *v.* A. Harker, in Rep. Brit. Ass. for 1885, 813.)

Most slates have originally been clayey sediments, and they consequently present much the same chemical composition as clays. It is notable that minute acicular crystals of rutile are often abundant. (On the origin of slate and of the rutile, *v.* W. M. Hutchings, Geol. Mag. 1890, 264, 316; 1891, 164, 304, 459.) Many secondary minerals, particularly chialstolite and the sericite variety of muscovite-mica, may be developed in slate, especially where it is invaded by igneous rocks. When this recrystallisation of the material is more or less complete, the rock presents a lustrous appearance on the cleavage surface, and is then known as a *phyllite* (*phyllade, Fr.*), forming a passage to the still more coarsely crystalline mica-schist.

The best slates occur in North Wales, where they have been worked since at least the sixteenth century. The principal quarries are those of Penrhyn, near Bangor, and Dinorwig, near Llanberis, where purple and green slates are worked in the Llanberis group of the Cambrian system. The slates quarried around Ffestiniog occur at a higher geological horizon, being referable to the Llandeilo beds. In Cornwall and Devon slaty rocks of Devonian age are abundantly developed, and are known locally as *killas*; they have been extensively quarried at Delabole and Tintagel in north Cornwall.

The following analyses are of: I, light blue slate stone from Penrhyn quarries, Bangor, North Wales (Cambrian age); II, grey-blue roofing slate from Delabole, Cornwall (Devonian, J. A. Phillips, Phil. Mag. 1871, 41, 95); III, green roofing slate from Honister Pass, Buttermere, Cumberland (Ordovician age; also MnO 0.39, BaO 0.02, CO₂ 4.51, SO₃ 0.14, P₂O₅ 0.12; T. M. Reade and P. Holland, Proc. Liverpool Geol. Soc. 1901, 9, 101; here several other analyses are given); IV, black roofing slate from Franklin quarry, Slatington, Pennsylvania (also CO₂ 3.67, P₂O₅ 0.17, MnO 0.09, BaO 0.08, FeS₂ 1.72, carbonaceous matter 0.59, SrO, Li₂O traces); V, red roofing slate from Hampton, Washington Co., New York (also P₂O₅ 0.05, MnO 0.10, BaO 0.04, FeS₂ 0.03); VI, sea-green roofing slate of Cambrian age from Brownell quarry, Pawlet, Vermont (also P₂O₅ 0.07, MnO 0.10, BaO 0.04, CO₂ 0.40, FeS₂ 0.22).

Analyses IV-VI by W. F. Hillebrand, U.S. Geol. Survey.

	I.	II.	III.	IV.	V.	VI.
SiO ₂	60.50	58.30	52.34	56.38	67.61	59.84
TiO ₂	—	0.23	1.05	0.78	0.56	0.71
Al ₂ O ₃	19.70	21.89	11.94	15.27	13.20	15.02
Fe ₂ O ₃	7.83	7.05	2.79	1.67	5.36	1.23
FeO	—	2.57	7.06	3.23	1.20	4.73
CaO	1.12	0.39	6.36	4.23	0.11	2.20
MgO	2.20	1.09	6.10	2.84	3.20	3.41
K ₂ O	3.18	2.45	1.03	3.51	4.45	4.48
Na ₂ O	2.20	1.18	1.78	1.30	0.67	1.12
H ₂ O	3.30	4.61	4.70	4.86	3.42	3.85
	100.03	99.76	100.33	100.39	100.00	100.17
Sp.gr.	2.88	—	2.77	2.78	—	—

Slates are not only valued as roofing material, but are used in large slabs for cisterns, flags, steps, tombstones, billiard tables, &c. Mantel-pieces are often constructed of slate, and enamelled to imitate marble or serpentine. Minor uses of slate are for splitting into school slates and cutting up into slate pencils. For pencils a soft fine-grained material is required, but as only small pieces are used there is no disadvantage in the rock being broken up by joints and cleavage-planes. The Skiddaw slate of the Lake District is used for pencils. The green slates of the Borrowdale series of Cumberland, which are used for roofing, consist chiefly of fine volcanic ash, in which perfect cleavage has been developed by compression.

Although the term 'slate' should properly be restricted to rocks which exhibit super-induced cleavage, it is often extended to fissile rocks which split along the original planes of bedding. Such thin flaggy rocks occur in the Oolitic system, and though not so thin and light as true slates, are used for the sake of their picturesque effect, especially in Gothic buildings. The *Stonesfield slates* of Oxfordshire and the *Collyweston slates* of Rutland are calcareous sandstones of this character. Such slates are not readily split into thin slabs when first quarried, but need exposure to a winter's frost in order to develop their latent fissility.

References.—J. A. Howe, The Geology of Building Stones, London, 1910. For the details of quarrying and dressing slate, *v.* D. C. Davies, Slate and Slate Quarrying, London, 1878. T. N. Dale, Slate Deposits and Slate Industry in the United States, Bull. U.S. Geol. Survey, 1906, No. 275; 1914, No. 586; H. K. Shearer, Report on the Slate Deposits of Georgia, Bull. Geol. Survey, Georgia, 1918, No. 34. L. J. S.

SMALT *v.* COBALT. For the constitution of Smalt, see Dubion, Compt. rend. 1921, 172, 972.

SMALTITE (*Speiskobalt, Ger.*). A mineral consisting essentially of cobalt diarsenide CoAs₂, of importance as an ore of cobalt. It has long been used for the preparation of smalt, hence the name smaltite. The crystals possess the same degree of symmetry as cobaltite (CoAsS) and iron-pyrites (FeS₂), but the pyritohedral faces are not often present, the form being usually the simple cube or the cubo-octahedron. Distinctly formed crystals are, however, exceptional, the mineral usually occurring as granular and compact masses. The percentage of cobalt required for the above formula is 28.2, but analyses rarely show over 20 p.c.; this is due to the isomorphous replace-

ment of cobalt by iron and nickel, and as the nickel increases in amount there is a gradual passage to the isomorphous mineral chloanthite (*q.v.*). The colour is steel-grey, and the streak greyish-black. The material is brittle; H. $5\frac{1}{2}$ –6; sp.gr. 6.4–6.6. Heated in a bulb-tube it gives a sublimate of metallic arsenic. When weathered the mineral alters to erythrite (cobalt-bloom), the characteristic peach-blossom colour of which is very often to be seen as specks and stains on specimens of smaltite, thus affording an easy means of recognising the mineral.

Smaltite occurs, together with ores of nickel, silver, and copper, in veins traversing granite and gneiss at Schneeberg, Annaberg, and Freiberg in Saxony, Joachimsthal in Bohemia, Wittichen in Baden, &c.; and in 1903 a similar occurrence was discovered at Cobalt on Lake Temiskaming in northern Ontario. In association with niccolite, barytes, and asbolite it occurs in veins traversing the Kupferschiefer (copper-slate) at Richelsdorf and Bieber in Hesse, and at Kamsdorf and Glücksbrunn in Thuringia. The occurrence of the mineral in the Saxon Erzgebirge led to the establishment long ago of cobalt colour works in this district. The still larger quantities recently found in Canada are far more than is required for the colour industry, and attempts have consequently been made to introduce metallic cobalt for the same purposes as nickel.

Safflorite is also cobalt diarsenide, but orthorhombic in crystallisation: it is thus dimorphous with smaltite and isomorphous with mispickel and marcasite. It occurs together with smaltite; in the massive form the two are practically indistinguishable, and no doubt the ordinary ore contains both minerals. The name safflorite is from saffire or safflor, a mixture of roasted cobalt ore and quartz used for colouring pottery. L. J. S.

SMELLING SALTS consist of mixtures of ammonium carbonate, or less often ammonium chloride, with a variety of essential oils. A large number of recipes are employed in their preparation, the following of which may be mentioned. Small glasses or bottles with ground glass stoppers are filled with pieces of sponge, previously well beaten, washed, and dried. These are then saturated with a mixture of ammonium chloride (9 parts) and oil of lavender (1 part); or the bottle may be filled with uniform sized pieces of ammonium carbonate and the above mixture poured over it. Other mixtures consist of: (1) 2 ozs. ammonia water, 7 drops of oil of lemon, 2 of oil of lavender, 4 of oil of bergamot; (2) 4 ozs. ammonia water, 15 minims of oil of rosemary, 15 of English lavender oil, 8 of oil of bergamot, and 8 of oil of cloves; (3) a coarse powder of normal ammonium carbonate is sometimes perfumed with bergamot oil (0.56 drm.), lavender oil (0.9 drm.), nutmeg oil, clove oil, rose oil (0.78 drm. each), cinnamon oil (2.82 drms.). This preparation is known as *white smelling salts*.

Violet smelling salts; coarsely powdered ammonium carbonate is moistened with a mixture of $2\frac{1}{2}$ ozs. of concentrated tincture of orris root, 1 drm. of spirit of ammonia, 3 drms. of violet extract, or the moistened carbonate is treated with as much of a mixture of 5 minims of oil of orris, 10 of oil of lavender flowers, 30 of violet

extract, and 2 fluid ozs. of ammonia water, as it will absorb.

Preston salt consists of a mixture of ammonium chloride and freshly-slaked lime, to which a suitable perfume is added.

Antiseptic smelling salts; often used for colds, hay fever, &c., consist of the following mixtures: (1) 1 lb. ammonium carbonate, 2 fluid ozs. ammonia solution, 4 fluid drms. eucalyptus oil, 1 fluid drm. lavender oil, 2 fluid drms. peppermint oil; (2) 120 grms. phenol, $1\frac{1}{2}$ fluid drms. eucalyptus oil, 4 fluid ozs. ammonia solution. (3) 10 parts menthol are dissolved in 78 parts of alcohol, and 12 parts of ammonia solution are added. Other antiseptic smelling salts are prepared by mixing 1 fluid oz. each of liquefied phenol, eucalyptus oil, iodine solution, and 2 fluid ozs. of ammonia solution; or 360 grms. of ammonium carbonate, 120 of camphor, 480 of phenol, 1 fluid dram of eucalyptus oil, 1 of lavender oil, and 2 of ammonia solution are mixed with a sufficient quantity of wood charcoal to form a suitable mass (*see* Encyclopædia of Receipts, Dick, 119; 20th C. Book of Recipes, Hiscox, 1907, 510; Chemisch. Technische Lexicon, Bersch, 1908, 630; Scient. Amer. Cyclopædia of Formulas, Hopkins, 1911, 873).

SMILACIN *v.* **SARSAPARILLA**.

SMITHSONITE (or Zinc-spar). Zinc carbonate (ZnCO_3) belonging with calcite, chalybite, &c., to the isomorphous group of rhombohedral carbonates, and an important ore of zinc. When pure it contains 52.1 p.c. of zinc, but this is often partly replaced isomorphously by iron and manganese, also, in smaller amount, by calcium, magnesium, copper, and cadmium. The mineral often occurs as brown, cavernous, or cellular masses without any prominent external characters; also as crystalline, botryoidal and stalactitic masses; sparry cleavage masses and crystals are less common. Sharply developed rhombohedral crystals of a fine apple-green colour were found in the old copper mine at Chessy, near Lyons. Sp.gr. 4.45, hardness 5. Smithsonite is a mineral of secondary origin derived from the alteration of zinc-blende. In some cases it may have been produced by the action of carbonated waters on zinc-blende; but in other cases the weathering of the blende has given rise to solutions of zinc sulphate, which in contact with limestone rocks have deposited zinc carbonate, calcium sulphate being removed in solution. Evidence of this metasomatic alteration is seen in the replacement of beds of limestone by smithsonite, and the frequent occurrence of pseudomorphs of smithsonite after calcite. Deposits of smithsonite were formerly mined in the limestones of the Mendip Hills in Somersetshire, in Derbyshire, and near Alston in Cumberland. Important deposits also exist in the province of Santander in Spain, Nerchinsk in Siberia, Missouri, New Mexico, Rhodesia, &c. Translucent material banded with pale green and blue colours from Laurion in Greece and Santander in Spain has been cut and polished for use as small ornamental stones. The ambiguous term calamine (*q.v.*) is sometimes applied to this mineral. L. J. S.

SMOKE and **SMOKE PREVENTION**. Smoke consists of liquids and solids condensing from heated products of combustion as they escape into the cool air, and in many cases solids carried

from the burning mass by the uprush of heated gases. If the products of combustion are entirely gaseous no smoke is formed.

The character of smoke varies with its source, and in most cases the nose is able to detect the character of the burning material from the smell of the condensing vapours in the smoke, so that tobacco smoke, coal smoke, wood smoke, the smoke from green vegetable matter, rags, animal matter or gunpowder have such distinctive characteristics that the sense of smell at once differentiates between them.

A. Trillat has found that smoke has strong germicidal properties. By treatment with the smoke from 2 grms. of sugar at 40°C. in a 12-litre vessel for 4 hours he found that *B. coli*, *B. subtilis*, and the bacteria of typhoid and cholera were destroyed, the action being due to the production of formaldehyde.

The form of smoke which is, perhaps, the most injurious, and to which we are most accustomed, is that produced by the use of bituminous coal as a fuel for manufacturing and domestic use, and which, with the growth in the population of the country and the prodigal methods of using the fuel, has created in our large towns atmospheric conditions that are little short of a national scandal.

When in the thirteenth century bituminous coal was first used for fuel purposes, the smoke to which it gave rise roused such indignation that a decree was passed in 1306 forbidding its use; but fuel had to be found, and the supply of timber proving insufficient, once more attempts were made to introduce it, but again public opinion led to its banishment during the reign of Queen Elizabeth. The third attempt, however, to bring it into use proved successful, and slowly the consumption increased, until the last century saw coal firmly established, not only as a fuel for domestic consumption, but also as the great source of power, and it was the possession of great stores of the fuel that gave England her commercial supremacy.

It was only in the latter half of the last century that the cumulative effect of smoke began to make itself appreciable, and the eighties and nineties were marked by a diminution in the hours of sunshine in the big cities, and by fogs of remarkable density; but such legislation as was enacted, the efforts of those interested in smoke abatement, and the large increase that has taken place in the use of coal gas for cooking and fuel purposes, have undoubtedly had some influence in a reduction of the nuisance. Certainly during recent years the fogs have not been of the same density or so frequent; and this has been due in no slight measure to efforts at smoke abatement.

Legislation has not been particularly effective, largely because proceedings can only be instituted for the emission of 'black' smoke, and then it has to be shown that 'the best possible means' has not been employed for avoiding smoke. Further, the smoke from domestic fires is excluded.

The factor which makes it difficult to obtain complete and therefore smokeless combustion of coal in a furnace, and almost impossible in an ordinary grate, is that bituminous coals of the kind used as fuel decompose rapidly at

temperatures above 400°, with the evolution of gases and condensable vapours, whilst a solid residue of carbon in the form of coke remains on the bars.

The gas is of the character of ordinary coal gas, and is easily burnt without smoke, whilst the coke residue also offers no difficulties, but the vapours, which on cooling condense to tar, are of so complex a nature, and under the influence of heat undergo such varied changes that their combustion is a most difficult problem, and it is the pitch, tar oils, and products from these that are the smoke-producing factors.

When fresh coal is thrown on the layer of incandescent fuel of a fire requiring replenishing, distillation at once commences. A ton of bituminous coal will yield about 11,000 to 12,000 cu. ft. of coal gas, and in addition tarry vapours which would bring the total to not less than 13,000–14,000 cu. ft. The coal gas presents little difficulty as far as smokeless combustion is concerned, beyond the large demand for air for combustion; it is the rapid production of volatile tarry matter which presents the greatest problem. A charge of 40 lbs. of coal produces about 240 cu. ft. of gas and vapour, and on an average these demand about 3500 cu. ft. of air for combustion. It is the difficulty of supplying and ensuring thorough admixture of this large quantity of air, and at the same time avoiding chilling, which are the main causes of smoke from bituminous fuel in industrial furnaces. In open grates there is no question of insufficient air; smoke in this case is largely due to the ignition temperature of the vapours not being reached, so that there is a process similar to ordinary destructive distillation, brown tarry smoke resulting.

Three essential conditions must be observed for the avoidance of smoke: sufficiency of air, thorough admixture, and maintenance of temperature. By skilful hand-firing smoke may be largely avoided, the general principle being the elimination of the great rush of gases and vapours which made it impossible to obtain the necessary admixture with a sufficiency of air. By coking the fuel on a 'dead plate' inside the fire door, so that distillation is slow and the products pass with air over the incandescent fuel on the bars, the coke being afterwards distributed over the grate; or by alternate firing on either the back or fore part of the grate, or on the right and left half-sections, great improvements may be achieved. Firing regularly at not too long intervals, with even distribution over the grate and with moderate amounts of fuel, will, with proper regulation of draught and air supply do much to reduce smoke.

Mechanical stokers are dependent upon a continuous feed of the fuel so that there is uniform production of the smoke-producing vapours and the air supply can be adjusted to give the best combustion whilst avoiding large excess, which reduces the boiler efficiency. Mechanically operated sprinkling stokers distribute the fuel continuously and evenly over the grate. Other forms are moving grates (chain grates) and moving bars, which slowly carry the fuel forward into the furnace; there are also stokers on the 'under-feed' principle where the raw fuel is carried forward beneath

the incandescent fuel on the grate and gradually works up as coking proceeds. The products of distillation therefore pass through the incandescent fuel bed and become completely burnt by the heated air which is readily accessible. A better boiler efficiency with accompanying fuel economy results with these mechanical arrangements, concurrently with the abolition of objectionable smoke. The latter is mainly *incidental* to the higher efficiency (arising from less excess air and higher carbon dioxide in the flue gases), although the claim is usually made that the fuel economy with improved boiler plant is due to the abolition of smoke.

When members of the Newton Committee visited Germany they were informed by the engineer at Krupps' works at Essen, where 400 boilers are installed, that he paid absolutely no attention to the question of smoke, but very great attention to efficiency. All the boilers seen at work were fitted with mechanical stokers and were practically smokeless.

Because of the widely different conditions under which coal is burnt, estimates of the losses through smoke and soot are very varied. Scheurer-Kestner in a careful examination of the flue gases from boiler furnaces found that the carbon lost never exceeds 1 p.c., the average being 0.5–0.75 p.c., on the carbon on the fuel. From researches in the laboratory of the United States Bureau of Mines (Bull. 49, 1912) it is concluded that the heating value of the solid particles represents from 1 to 3 p.c. of the heat units of the coal used. C. E. Stromeyer found that very dense black smoke consisted of waste gases and about 1 p.c. of unburnt carbon, which represented a loss of efficiency of about 2 p.c. Roberts-Austen, from experiments with forty different kinds of domestic grates, found the percentage loss of coal as *soot* was rather over 6 p.c., a figure in close agreement with results by J. B. Cohen. Soot, however, generally contains a high proportion of ash (*see* Table I.).

The Committee on Noxious Smoke and Vapours Abatement (Lord Newton's Committee), appointed by the Minister of Health, in their Report (1921) take this same figure of 6 p.c., and say that 'taking 40½ million tons as the amount of coal burnt annually in the United Kingdom in its natural condition for domestic purposes, the loss amounts to 2,430,000 tons of potential fuel.'

This figure of 6 p.c. is probably an over-estimate, and appears to be based upon the assumption that the whole of the distillation products, other than the uncondensable gases, escape unconsumed, for, according to the Fuel Research Board's investigations on low-temperature carbonisation, a ton of coal yields 13–17 galls., say 5–7.2 p.c. by weight, of tar oils, and the distillation phase in a domestic grate is undoubtedly of the low-temperature order. Even although the above estimate of loss of potential fuel may be exaggerated, there can be no question that the annual loss is very large, and there are concomitant losses of a high order. Household washing costs in big cities are much greater than in rural districts, and involve further consumption of fuel; there is damage to buildings and added costs for painting and decorating, and undoubted impairment of health. Statistics laid before the Committee

showed that the number of deaths from pulmonary and cardiac diseases increased in direct proportion to the increase in duration and intensity of smoke fogs.

If the products escaping from a fire soon after being fed with fuel be collected in the flue they are found to contain—

1. Tar vapour;
2. Water vapour;
3. Tarry carbon particles;
4. Particles of ash;
5. Flue gases.

The tar vapour in the smoke is formed by distillation from the coal, whilst the solid carbon deposits coated with tar, soot, are a secondary product of the incomplete combustion of the tar vapour, and are formed by the cooling of the flame above the fire by the air drawn in by the chimney draught, which also carries off from the fire particles of ash and coal-dust.

Most samples of soot contain a good deal of mineral matter, partly the ash of the coal, and partly consisting of ammonium salts, such as the sulphate and chloride. The well-known manurial value of soot is largely due to these salts. The organic matter consists chiefly of carbon and tarry substances, together with sulphur and nitrogen compounds. Pyridine bases are present, and Trillat has detected the presence of formaldehyde (0.28–0.35 p.c.). Many samples are strongly acid. The composition of soot from various sources is given in Table I.

Where the draught is strong, as in boiler plants, the proportion of mineral matter is high. This may be due to two causes: mechanical carrying away of the ash of the fuel, and the burning away of tars and carbonaceous substances at the high temperature of the boiler flues. The condensation of tarry matter and ammonium salts will also be dependent on temperature, points well shown in the analyses given. Calculated on the ash-free soot the tarry constituents are lower in the kitchen soots than in those from open grates, and they are only present in very small amounts in the boiler soots, increasing in the higher parts of the chimney. There is apparently almost simple distillation with open grates, whilst with the stronger draught and higher temperatures in industrial furnaces partial combustion of the tar occurs, with the formation of much free carbon, which would account for dense black smoke.

In the flue gases, the water vapour and gases, other than the nitrogen and oxygen, are formed by complete and incomplete combustion, and amongst them are to be found sulphur compounds, such as sulphuretted hydrogen and sulphur dioxide, the first formed during the distilling period when coal has just been fed on to the fire, and the latter during the combustion. Both these compounds are due to the sulphur always present in the coal, and whilst the former blackens white lead paint and tarnishes silver, the sulphur dioxide dissolving in water oxidises to sulphuric acid, which is far more actively injurious, corroding and destroying metal work and building materials, retarding the growth of vegetation and finally killing it.

Bituminous coal contains from 0.5 to 3.5 p.c. of sulphur, chiefly in the form of iron pyrites, and it is generally assumed that—as about

TABLE I.—ANALYSES OF SOOT.
(Cohen and Ruston, Jour. Soc. Chem. Ind. 1911, 1360.)

	Domestic								Industrial		
	Sitting-rooms					Kitchens			Steam boiler		
	Aver- age	Aver- age	Height in chimney			Aver- age	Aver- age	Height in chimney			
			5 ft.	20 ft.	35 ft.			Base	70 ft.	Top 110 ft.	
<i>Composition of whole soot :</i>											
Ash	18·16	20·22	5·09	4·97	4·94	17·80	27·34	75·04	66·04	61·80	
Tar	25·91	15·68	34·90	37·20	40·40	12·50	10·20	0·09	0·80	1·66	
Carbon	40·50	47·75	36·50	34·10	37·20	52·30	45·91	16·66	21·80	27·00	
Hydrogen	4·37	4·85	3·50	3·50	3·50	3·70	2·18	0·86	1·44	1·68	
Nitrogen	4·09	5·57	6·89	6·04	5·05	4·11	2·33	0·00	1·18	1·21	
Sulphur	2·99	2·32	2·18	2·56	2·45	2·20	1·46	2·07	2·58	2·84	
Chlorine	5·19	6·46	9·07	6·41	4·96	1·35	4·64	3·11	1·46	1·60	
<i>Composition on the ash-free soot :</i>											
Tar	31·60	19·65	36·80	39·20	42·10	15·20	14·05	0·36	3·19	4·35	
Carbon	49·50	59·70	38·50	35·80	39·10	63·50	63·00	66·80	64·00	70·60	

16,000,000 tons of coal are used in London annually, the sulphur is all converted into sulphuric acid, and that anything from half a million to a million tons of acid is so formed in the air of London in the course of the year. This is undoubtedly an exaggeration, as during the smoke-forming period of combustion a large proportion of the sulphur comes off in combination with hydrogen, and escaping unburnt, can be detected in the chimney gases by its action on lead acetate paper, whilst some of the sulphur dioxide is removed by rain before the oxidation to sulphuric acid is completed.

The sulphur compounds in the air vary with the state of the atmosphere, so that on a breezy bright day, even in the heart of London, 100 cu. ft. of air may contain only 0·015 grm., whilst during a dense fog they may rise to 0·24 grm., and it is clear that as the smoke helps the formation of the fog, and this in turn prevents diffusion and removal of the impurities in the air, the prevention of smoke should go far towards purification of the town atmosphere.

Deleterious as is the effect of sulphuric acid in the air and rain upon the growth of vegetation, it is found that the soot in town air is even more so, as the small masses of spongy carbon that are called ‘blacks’ have the power of absorbing and concentrating sulphuric acid, so that they may contain 4–8 p.c. of it, and when the growing plant gets coated with a tarry film rich in ‘blacks,’ not only are the functions of the pores of the plant deranged, but the acid is brought in a concentrated form in contact with the leaf surface.

Smoke once formed finds its way from the chimney into the atmosphere, and is rapidly diffused through the air by means of currents, and it is manifest that if there were no means of removing it, the air would soon become perfectly opaque from its accumulation in large quantities. When, however, rain falls

it rapidly washes the air free from suspended solid and liquid impurities which constitute the visible portion of smoke. Snow is even more efficacious than rain in this respect ; where the snow has fallen on the glass roof of a greenhouse it will be noticed that when it melts it leaves behind a black deposit, consisting of the solid matter which it has collected during its passage through the air. An analysis of a deposit of this character formed on the glass roofs of some orchid houses at Chelsea serves to show the nature of these solid impurities—

Carbon	39·00 p.c.
Hydrocarbons	12·30 „
Organic bases	1·20 „
Sulphuric acid	4·33 „
Ammonia	1·37 „
Metallic iron and magnetic oxide	2·63 „
Other mineral matter, chiefly silica and ferric oxide	31·24 „
Water not determined.	

In cases where long drought prevents the rapid clearance of the air by this means, the heavier of the solid particles settle by gravity, whilst the particles of carbon and carbonaceous organic matter are slowly oxidised by the oxygen and ozone into carbon dioxide, in which form vegetation removes them from the air.

The solid particles suspended in air are, however, by no means confined to the products of our improper use of bituminous fuel, and mineral matter from the dust of roadways, and organic matter from animal and vegetable life, play their part in rendering town air deleterious to health, but it is the smoke ‘dirt’ that is the most injurious factor.

Systematic investigation of the soot and dust fall has been established in many of the principal towns under the direction of the Meteorological Office. Standard collecting funnels of 4 sq. ft. area are employed and determinations made

of the volume of water collected, total solids, tarry matter, non-tarry carbonaceous matter, sulphates, chlorides, ammonia, and lime. Table II. summarises the principal results from the early series for ten important towns.

The very heavy deposits of the large industrial towns are in striking contrast to those of purely residential towns, like Malvern and York. The aggregate for the tarry and carbonaceous deposit in the industrial towns amounts to many tons

TABLE II.—DEPOSIT OF SOLID MATTER IN WINTER MONTHS.
(October to March.)

Town	Tons per square mile				Percentage soluble constituents	Percentage insoluble constituents	Percentage composition of the insoluble solids		
	Total	Soluble	Insoluble (tar, soot, ash)	Tar and soot			Tarry	Carbonaceous	Ash
Oldham . . .	532	168	364	114.5	31.6	68.4	1.5	30.0	68.5
Birmingham . . .	382	130	252	70.0	34.0	66.0	1.2	26.6	72.2
Bolton . . .	346	215	131	32.5	62.2	37.8	1.2	23.6	75.2
Sheffield (Attercliffe) .	321	128	193	63.5	39.9	60.1	1.3	31.6	67.1
Liverpool . . .	286	119	167	39.4	41.6	58.4	2.6	20.9	76.5
Newcastle . . .	265	109	156	61.0	41.2	58.8	1.3	37.6	61.1
Manchester (Technical School) . . .	263	107	156	53.0	40.7	59.3	1.1	32.6	66.3
London (Golden Lane)	249	121	128	50.0	48.6	51.4	0.9	38.1	61.0
York . . .	158	80	78	25.5	50.3	49.7	2.0	30.5	67.5
Malvern . . .	32	26.1	5.9	2.05	81.8	18.2	0.8	24.0	65.2
Average . . .	—	—	—	—	47.2	52.8	1.4	30.6	68.0

per sq. mile ; these constituents may be regarded as wholly due to the imperfect combustion of coal, and it must be remembered that the deposit collected represents only a portion of the unconsumed material discharged into the air, since a considerable part must be carried into outside areas by the action of winds. A striking feature is the amount of soluble material brought down, approximately half the total, although the average is greatly exceeded at Malvern and to a less extent at Bolton. Another striking feature is the small amount of tarry matter. The ratio of carbonaceous material to tar in these deposits is 22:1. From the table of the composition of soots the like ratios are : sitting-rooms, 1.3:1 ; kitchens, 4.3:1 ; steam boiler, 25.5:1.

The smoke from our grates is naturally discharged at a lower level than that from factory shafts, with the result that it probably has a greater effect on our general health and buildings than the higher layers of smoke, which travel for miles with the wind, and which act more by darkening the sky and cutting off the sun's rays. It is also clear that the low-level smoke will not extend so far from the point at which it is formed, as contact with buildings and vegetation rapidly robs it of the tarry products, with the result that in a smoky town like Leeds it has been shown that at 1 mile away the solid impurities have fallen to one-half, and at 2½ miles to one-sixth.

Injurious as are the direct effects of smoke on health and property, they are small as compared with those brought about by dense fog, which may to a great extent be attributed to smoke, partly by helping its formation and partly by retarding its dispersion.

Fog, whether it be in the form of white mist

which is found in the country, or the yellow variety which we know so well in towns, is formed by the condensation of water vapour from the air, and this is brought about by any cause which rapidly cools a large volume of moist air.

The air of towns where much coal is used also contains the volatile tarry matter distilled off during the imperfect combustion, and this condensing with the moisture coats it on the outside with a thin film, which does much to prolong the existence of the fog, as when the temperature of the air again rises, the clean mist once more evaporates into the atmosphere, but the tar-coated yellow fog has its power of evaporation retarded to an enormous extent. Experiments made by Sir E. Frankland show that the evaporation of water in dry air is reduced nearly 80 p.c. by blowing some smoke from burning coal on to its surface.

Many estimates of the relative amount of pollution due to manufactories and to the domestic grate have been made, but as the question of what is the ratio of smoke production from the various sources varies enormously with the locality, no very satisfactory conclusion has been arrived at.

With regard to London, Sir Napier Shaw's estimate that 70 p.c. of the smoke is due to the domestic fire would probably be about correct, but in Sheffield or Birmingham the figures would most likely be reversed. The Newton Committee Interim Report states that even in industrial centres domestic chimneys contribute at the least 50 p.c. of the total smoke nuisance, and this is considered as in all probability a very conservative estimate. Domestic smoke is produced throughout the whole length and breadth of the land, whereas the factory chimney

is to be found mainly in the more limited area of the manufacturing districts.

Practically all the advances of late years have been in fuel consumption on the large scale, and the improvements brought about by stoking machinery and attention to air supply have been great, whilst some of the largest manufacturers have demonstrated not only the ease of obtaining smokeless factory shafts, but also the economy that accompanies them.

The methods that could be adopted for reducing the production of smoke from domestic sources are :—

1. The use of bituminous fuel in special grates ;
2. The use of solid smokeless fuel ;
3. The use of gaseous fuel ;
4. The combined use of gas and coke ;
5. Central heating by steam, water, or hot air.
6. Electric heating.
7. Mineral oil stoves.

Discussing the possible methods which might be employed to minimise the production of smoke in new houses, the Newton Report makes the following comments :—

Raw coal burnt in open grates inevitably produces smoke which may almost entirely be eliminated by the substitution of smokeless heating agents.

The witnesses have almost without exception condemned the old-fashioned kitchen range and back boiler (Yorkshire and Lancashire open range) which attempts to warm a room, supply hot water and heat the oven and hot plate, as inefficient, wasteful of fuel and labour, and productive of smoke.

If a coal grate is to be installed it is clearly desirable that it should be as efficient as possible, in the interests not only of fuel economy, but also of smoke abatement, since an efficient fire burns less fuel and therefore emits less smoke.

Where coal or coke grates are installed the following conditions should be observed :—

- (a) The grate should not be recessed.
- (b) Adequate means should be provided for controlling the rate of combustion by regulating the draught. In addition to the usual regulator below the fire a damper should be fitted to control the draught up the flue.
- (c) Wherever practicable, flues should be built on inside and not on outside walls.

Ordinary gas-coke.—A large quantity of coke is at present available, and this could be increased almost indefinitely if the demand were created. There is little difference in price between coke and coal, and coke has the great advantage of being smokeless. Good quality coke, when burnt in a suitably constructed grate, gives a brightly glowing fire and a higher radiant efficiency than coal. Though difficult to kindle, combustion can readily be started either with raw coal or preferably by the aid of a gas jet. Coke is an economical fuel for heating water both in a closed and open stove and for use in certain types of kitchen ranges.

Low-temperature coke.—The quantity of low-temperature coke at present on the market is very small. It is possible that by some modified process of carbonisation it may become commercially practicable to produce on a large scale a solid smokeless fuel, which is free from the

disadvantages of much of the coke now on the market.

When and if such a solid smokeless fuel can be produced on a sufficiently large scale and at a low enough price as compared with other fuels, it may be practicable and desirable to legislate against the burning of raw coal in domestic grates, and thus eventually solve the problem of domestic smoke.

Gas.—The principal advantages of the use of gas are its efficiency (better utilisation of the heat), cleanliness, and the ease with which it can be turned off when not required (intermittent use). These advantages often more than compensate for the higher price of gas when measured by thermal units.

The quantity of sulphurous and sulphuric acid fumes emitted by gas fires is much less than from coal fires—a point of great importance in view of the evidence we have received with regard to the deleterious effect of these acids, even apart from smoke, upon buildings and stonework.

The Committee was satisfied that gas cookers and gas fires are thoroughly hygienic when properly installed, and that they are more economical than coal fires for intermittent use. It also appears that gas fires would lead to considerable reduction in building costs by eliminating the chimney breasts and stacks and substituting smaller flues within the wall.

Several witnesses advocated gas as the best available fuel, the cooking to be done by a gas-cooker, the rooms warmed by gas fires, and the hot water supplied by a gas boiler. The advantage of a gas boiler is that it can be used in summer when an open fire is not required, and that it is clean and convenient.

As a modification of the 'all gas' house a separate coke-fired boiler can be installed for heating water; for a continuous supply this would be decidedly cheaper.

Electricity.—Electricity has also been urged as an efficient method for cooking and for warming rooms, but not, owing to its present cost, for heating water.

From a hygienic and labour-saving point of view electric cooking and heating has much to commend it, but we hesitate to advise its adoption on the evidence before us, in view of the high price at present charged for electricity in many localities.

If electric current can eventually be supplied at a much cheaper rate than to-day, full advantage will no doubt be taken of it in designing the heating and cooking arrangements of houses.

Mineral oil.—Oil fuel is more costly than either coal, coke, or gas; but when these are not readily available, as in country districts, oil may be and is frequently used for cooking.

(A well-designed oil stove is one of the most efficient forms of heater, and this would considerably reduce the adverse cost balance against oil. With an oil stove kept in a proper state of cleanliness, and using a good quality oil, there is practically an entire absence of smell.—J. S. S. B.)

The following is a summary of the recommendations of the Newton Committee :—

- (1) Subject to the opinion previously

expressed with regard to the future possibilities of electricity as a heating agent, wherever a supply of gas is available, a gas cooker should be installed in lieu of a coal range.

(2) The cheapest and most efficient method of providing a supply of hot water, where a central supply is not practicable, is by a coke-fired boiler.

(3) A central hot-water supply for detached houses, where practicable, is a desirable system, if it can be provided at a moderate cost.

(4) For tenement houses a central supply of hot water is quite practicable and should be provided universally.

(5) The system of installing separate central-heating plants in each house heated by coke or anthracite should be employed far more widely than is at present the case.

(6) As far as practicable gas fires or hot-water radiators (or electric radiators subject to the question of cost) should entirely supersede the old-fashioned open coal fire, adequate means for proper ventilation being provided.

(7) There is still a strong prejudice in many quarters in favour of an open coal fire, and we therefore limit our recommendation to this extent, namely, that in none of the houses built with the assistance of the Government subsidy should more than one, or, in exceptional circumstances, two coal grates be installed.

Wherever coal ranges and coal grates are installed they should be of a type adapted to the use of coke as well as of coal. Adequate means of regulating the draught should in all cases be provided.

In conclusion, the Committee desired to emphasise the fact that the present housing situation afforded a unique opportunity for constructive reform with regard to the heating, cooking, and hot-water supply arrangements in domestic dwellings. Reformers in the past have always been confronted with established facts. It was urged, and not without point, that it was impracticable to attempt smoke abatement by altering existing appliances installed in houses constructed on old-fashioned lines. But the position has changed, and having regard to the serious damage caused by domestic smoke and at the same time to the great improvements which have been introduced into modern systems of heating, the Committee wish strongly to urge on those who are engaged in the preparation of new housing schemes, the great importance of providing, as far as practicable, smokeless arrangements for warming rooms, supplying hot water, and for cooking.

Following the issue of the Newton Report, Bills introduced into Parliament (1922, 1923) on behalf of the Ministry of Health indicated that at least some of the important suggestions made for reducing the smoke nuisance are likely to be adopted in the near future, *e.g.* smoke, no matter of what colour, if emitted in quantities giving rise to a nuisance should come under the Acts; 'smoke' should include 'soot, ash, grit, and gritty particles.' Another clause suggested that with new buildings, *other than private dwelling houses*, the heating arrangements should be of such design that smoke was prevented or 'reduced.' Further very considerable increases in the maximum penalties for offences were suggested.

J. S. S. B.

SMOKELESS POWDER *v.* EXPLOSIVES.

SNAKE VENOMS. That of the cobra contains a nerve poison, *ophiotoxin*, which paralyses the respiratory centre and has, according to Faust (Arch. exp. Path. Pharm. 1907, 56, 236), approximately the composition $C_{17}H_{26}O_{10}$, and resembles the saponins in physical properties. Cobra-venom further contains a hæmolysin, which, according to Manwaring (Zeitschr. Immunitätsforsch. 1910, 6, 513), is a lecithinase, that is, an enzyme which splits off one of the fatty acid groups of the lecithin of the victim's blood; partially hydrolysed lecithin is known to be hæmolytic. By gradually immunising horses against snake venoms, Calmette has produced anti-venins resembling bacterial anti-toxin sera, but since snake venoms are highly specific, they each require their own particular anti-venin.

G. B.

SNOW-BRUSH WAX *v.* WAXES.

SOAMIN. Trade name for crystallised sodium *p*-arsanilate (atoxyl). *V.* ARSENICALS, ORGANIC.

SOAP. The term 'soap' in its widest sense includes all salts of fatty acids. In ordinary language, as also in commerce, the term is applied almost exclusively to that mixture of alkali salts and water which is sold as soap.

It is most convenient to subdivide the soaps into the two main classes, viz. (1) *Salts of the alkali metals; water-soluble soaps.* (2) *Salts of the alkaline earths and heavy metals; water-insoluble soaps; metallic soaps.*

Ammonia soaps, which as yet are of no great commercial importance, would be classed with the water-soluble soaps.

(1) SALTS OF THE ALKALI METALS; WATER-SOLUBLE SOAPS.

According as to whether the base used for the saturation of the fatty acids be sodium hydroxide or potassium hydroxide, we differentiate between *hard soaps* (soda soaps) and *soft soaps* (potash soaps). The former may contain small quantities of potash soaps (as is the case in high-class shaving and other soaps), whilst the latter may also contain some proportion of soda (as is the case in soft soaps made in summer), but it is convenient to found the classification on the quantity of the preponderant base, as, indeed, is done in practice.

The fatty raw material for commercial soaps may be furnished by any oil or fat of vegetable or animal origin. Thus an enormous variety of soaps can be, and, indeed, are produced on a large scale. But not every oil and fat yields a soap fulfilling the demands made on it for household, toilet, and manufacturers' purposes. Broadly speaking, it may be stated that the vegetable drying oils and marine animal oils are, on account of their consistence, best suited for the manufacture of soft soaps. Also some of the semi-drying oils (maize oil, rape oil) lend themselves especially for this purpose. Solid fats are used preponderantly for making hard soaps; into this category fall also the non-drying oils. Semi-drying oils, as typified by cotton-seed oil, may be used as stock material in admixture with other suitable oils and fats for both soft and hard soaps.

The art of the soap-maker consists in blending

the raw material at his disposal in such a manner as to produce that soap which is most suitable for a given purpose.

Rosin is largely used in conjunction with fatty material in the manufacture of both hard and soft soaps.

1. Hard Soaps—Soda Soaps.

The earliest processes of manufacturing hard soap (described by Pliny) consisted in boiling oils and fats with causticised wood ashes, the potassium carbonate contained therein being converted into potassium hydroxide by boiling with lime. The potash soaps so obtained were converted into soda soaps by treating the soap paste repeatedly with common salt.

Later on the wood ashes were replaced by 'soda ashes' obtained by burning seaweeds ('barilla,' 'kelp'). The manufacture of sodium carbonate by the Leblanc- and the ammonia-processes almost completely extinguished the use of barilla and kelp, and the soap-maker was thereby enabled to obtain manufactured soda (soda ash, sodium carbonate), which he causticised himself in the same manner as that employed for wood ashes. Thus the caustic soda required for the saponification of oils and fats was actually manufactured in the soap works, and is, to a large extent, still being produced by the soap manufacturer.

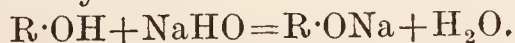
The development of modern chemical industry led to the production of solid sodium hydroxide in alkali works (started in England, 1850), so that the soap-maker has at present the choice of either buying sodium hydroxide in the solid form or himself manufacturing sodium hydroxide solution ('caustic lyes') from soda ash, by causticising sodium carbonate, and subsequently concentrating the dilute sodium hydroxide solution in vacuum evaporators of simple or multiple type (for illustrations, see GLYCERIN).

The following two processes for the production of hard soaps from oils and fats on a manufacturing scale are chiefly in use: (A) *Soap-making by the cold process*, and (B) *Soap-making by the hot process*. More recently a third process has been introduced on a limited scale, viz. (C) *Soap-making by double decomposition of lime soaps and sodium carbonate*.

Under the head of 'hot process' falls also the method of making soap from fatty acids or 'soap stock fatty acids.'

For the theory underlying the process of soap-making from oils and fats, see GLYCERIN and SAPONIFICATION.

The theory of soap-making from fatty acids is expressed in its simplest form by the following equation, wherein R denotes the radicle of any suitable fatty acid—



For the physical properties of the soaps of the several fatty acids, their solubility, their behaviour towards water (*hydrolysis of soap*), caustic alkalis, carbonates of the alkalis, glycerin, alcohol, and neutral salts, the reader may be referred to the article OILS, FIXED, AND FATS and to Lewkowitsch, Chem. Techn. vol. i.

(A) Soap-making by the Cold Process.

The oils and fats most suitable for the manufacture of soaps by the cold process are those

belonging to the coconut oil group, as they possess the property of being converted into soaps on being stirred together with concentrated sodium hydroxide solutions of approximately the sp.gr. 1.35. The plant required for this manufacture is of the simplest construction, and merely consists of an iron or wooden frame into which the fat, previously brought to a temperature of about 35°, is placed; the fat is then stirred, whilst an accurately measured quantity of sodium hydroxide solution of sp.gr. 1.35 is run in. The frame is covered and allowed to stand, when the mass develops some heat, sufficient to complete the process of saponification within 24 hours.

The simplicity of this process naturally led to the market being flooded with 'cold' soaps prepared by unskilled operators, so that these soaps contained a considerable excess of sodium hydroxide, or unsaponified fat, side by side with free sodium hydroxide. The prejudice which has arisen against this class of soap is, however, unfounded, as it is not difficult, by careful working, to prepare practically neutral soaps. For this purpose the quantity of sodium hydroxide required for saponification must be calculated from the saponification value of the fatty material.

These soaps are not readily 'salted out' by brine; hence they can be used for washing with sea-water (*marine soaps*). By incorporating with coconut oil certain proportions of olive oil, lard, tallow, &c., these oils and fats can also be saponified in the cold.

Soaps so prepared naturally contain the whole amount of glycerol that results from the saponification of the oils and fats. The theoretical composition of a soap made from coconut oil, having a saponification value of, say, 240 by the cold process is the following—

Fatty anhydrides	54.50 p.c.
Combined sodium oxide, Na ₂ O	8.86 „
Glycerol, water, and small quantities of inorganic salts (by difference)	36.64 „
	100.00

Cold soap cannot be conveniently made on a practical scale from fatty acids or soap stock fatty acids, as in consequence of the immediate combination of fatty acid with sodium hydroxide, lumps are formed which occlude the uncombined materials. For this reason, fats containing notable amounts of free fatty acids are unsuitable for the manufacture of cold soaps.

Castor oil resembles the fats belonging to the coconut oil group in being able to form 'cold' soaps. The further property of castor oil of imparting translucency to soap has also been made use of in the manufacture of inferior cold soaps, and complete transparency is obtained by the addition of sugar solutions together with sodium silicate solution. On the Continent large quantities of cheap transparent soaps of this kind are made. They must not be confounded with the high-class transparent soaps described below.

(B) Soap-making by the Hot Process.

In soap-making by hot processes, either natural oils and fats or the fatty acids derived therefrom are used.

(a) *Soap-making from natural oils and fats with sodium hydroxide.*—The process of soap-making by boiling glycerides with sodium hydroxide solutions is used on the most extensive scale, and is practically the only process which yields soaps of uniformly good quality, colour, and hardness, and at the same time the largest amount of glycerol obtainable from the raw material by means of comparatively simple operations.

In this process the oils and fats are introduced into a cylindrical or square iron vessel—soap kettle, soap ‘copper,’ soap pan—and churned up by means of steam, when a dilute sodium hydroxide solution is run in, which assists the emulsifying of the fat and induces rapid hydrolysis.

It is necessary to commence with a dilute solution of sodium hydroxide, as in the case of oils and fats, with the exception of the oils belonging to the coconut oil group and of castor oil, a strong solution ‘cuts’ the soap-paste, much as does salt solution.

The mass in the soap-pan at this stage consists of a mixture of sodium salts of the fatty acids with water, in which the glycerol formed in the course of hydrolysis and the excess of sodium hydroxide are dissolved.

It is necessary to employ an excess of sodium hydroxide to obtain complete saponification. Experiments made by the author with his assistants Clapham and De Greiff have shown that by using the theoretically required quantity of sodium hydroxide an equilibrium is established between soap and unsaponified fat, so that the resulting mass contains such notable quantities of unsaponified fat that the soap would be unsaleable.

In order to convert the soap-paste into commercial soap, it is necessary to separate the sodium salts of the fatty acids from the excess of sodium hydroxide and of water by adding salt, whereby the soda soaps are thrown up. On allowing the mass to stand, two layers are obtained: (1) a lower aqueous layer, containing salt, glycerol, and excess of sodium hydroxide; (2) an upper curdy mass of soap granules, retaining about 30–35 p.c. of water. The lower layer is drawn off, and worked up for the recovery of the glycerol contained in it (*see GLYCERIN*). The curdy soap granules left in the pan are boiled up with water (‘closed’), so as to form a homogeneous paste, which is again boiled with a little sodium hydroxide to ensure complete saponification, and again separated into two layers in the manner described above. The soap is once more treated in the same manner, to remove impurities which impair its colour; in some cases it is boiled with a somewhat concentrated solution of sodium hydroxide (‘strengthening change’) and ‘salted out’ again to a ‘curd.’ Finally the ‘curd’ is ‘fitted,’ *i.e.* brought into the condition of finished soap.

The art of the soap-maker consists in so ‘fitting’ the soap that it contains just the proper amount of water (which may be called the ‘water of constitution,’ *see below*), and is still ‘open’ enough to allow the intermingled heavier aqueous solution, as also the impurities (which consist to a notable extent of metal [iron, copper], salts of fatty acids) to settle out. After

the mass has been allowed to rest for a few days, there is found at the bottom of the soap-pan a small amount of alkaline solution (which has separated out on cooling, *see below*), above which rests a layer of dark soap, intermixed with salt solution, containing the excess of sodium hydroxide used. The dark colour is chiefly due to metallic soaps. This layer is termed in practice ‘nigre’ (*i.e.* black, a term taken from the Marseilles soap-makers). Above this rests the bulk of the finished soap, ‘neat soap.’ It is covered on the top by a thin layer of solidified soap of a spongy nature, owing to the occlusion of air, which on rising gradually to the top of the mass during settling became entangled there on cooling.

The excess of caustic alkali in the ‘neat’ soap should be very small; its amount depends on the care used in the manufacturing operations.

The finished ‘neat’ soap, whilst still warm, is run into soap crutching (mixing) machines (holding from 12 to 15 cwts. of soap), wherein perfumes and colouring matters are incorporated with the soap (if desired), and thence into soap frames, in which the warm mass is allowed to cool. (In the south of Europe the finished soap is run on to a cemented floor divided off by boards into suitable compartments, about 12–14 ins. high. For the best class of household soaps the cemented floor is covered with paper.)

The soap in the frames requires a few days to solidify. The sides of the soap-frames are then removed, and thus a rectangular soap block is left. This block is cut at first into slabs, which are then divided into bars and tablets, to be placed on the market.

The process of solidification of the soap being a somewhat lengthy one, cooling machines have been introduced, and enjoy, especially on the Continent, a certain vogue. In this country, however, such cooling machines have found very limited use. For the best household soaps the process of cooling in frames has maintained its supremacy.

Pure commercial soda soaps made by the process described contain practically 30 p.c. of water, and not more than 63–64 p.c. of fatty acids. Such a soap is termed ‘genuine soap.’ The theoretical composition of a genuine soap made from neutral glycerides having the mean molecular weight of about 860 (tallow, olive oil, &c.), is as follows:—

Fatty anhydrides	61·60 p.c.
Combined sodium oxide, Na ₂ O	7·18 „
Water, including small quantities of inorganic salts and glycerol (by difference)	31·22 „
	<hr/> 100·00

In the course of a long series of experiments which the author carried out on a large scale on many tons of varied fatty materials, with the object of producing a commercial soap having a higher proportion of fatty acids than 63–64 p.c., he was never able to obtain a commercial soap of the desired higher percentage. Hence, he adopted the view that this proportion of water might be termed ‘water of constitution,’ inasmuch as a commercial soap having less water cannot be obtained in the soap-kettle.

The statement made by Merklen that he obtained soaps with higher percentage than 63-64 p.c. has been refuted by the author as impossible (*see* Lewkowitsch, J. Soc. Chem. Ind. 1907, 590; Jahrbuch d. Chem. xvii. 415; Lewkowitsch, Chem. Techn.).

Fischer (Chem. Soc. Abstr. 1922, ii. 430), from a study of the water taken up by fatty acids, drew the conclusion that the water in the soap gel or curd is in solution. R. Zsigmondy (Zeitsch. physikal. Chem. 1924, 108, 303), on the basis of the vapour pressure-concentration diagram, contends, however, that the water is neither in solution nor present as water of crystallisation, but is enclosed in capillaries formed by the framework of fine needle-like crystals of the soap, ultra microscopic in two dimensions which are known to compose the curd (Zsigmondy and Bachmann, Chem. Soc. Abstr. 1912, ii. 1149; McBain and Laing, T., 1919, 115, 1279; 1920, 117, 1506; Chem. Soc. Abstr. 1924, 126, ii. 391).

(b) *Soap-making from fatty acids (Soap stock fatty acids).*—This process of soap-making was first suggested by Chevreul, and has, indeed, been in practical use ever since the stearine candle industry was established, the manufacture of soap from oleic acid—the by-product of the stearine candle industry—affording a natural outlet for this by-product. Since fatty acids are capable of expelling carbonic acid from sodium carbonate when boiled in aqueous solution, soap can also be made by boiling fatty acids with sodium carbonate.

The initial manufacturing operation is, therefore, practically tantamount to neutralising the fatty acids with sodium hydroxide or with sodium carbonate, as the case may be. The precaution must, however, be taken that the aqueous solution of sodium hydroxide or sodium carbonate is put first into the soap-pan, and that the oleic acid is allowed to run in slowly while the mass is kept boiling, so as to avoid formation of lumps of soap. If sodium carbonate be used, the boiling must be conducted with great circumspection, so as to facilitate the evolution of carbonic acid and to prevent boiling over of the 'fobbing' mass.

In consequence of the high price which glycerin has reached, special 'deglycerinising' works were established on the Continent, and the manufacture of soap from 'soap stock fatty acids' has gained some extension, notably in small soap-works on the Continent, one of the chief advantages claimed for this raw material being the saving of cost afforded by using sodium carbonate in place of sodium hydroxide—of course, as far as the proportion of free fatty acids permits.

The soap stock fatty acids are prepared by the saponification processes mentioned under Nos. 2, 5c, and 6 in the article SAPONIFICATION.

The neutralisation of the soap stock fatty acids is carried out in the same manner as described above for oleic acid. The sodium carbonate solution must be heated first in the soap-pan, and the soap stock fatty acids are introduced in small quantities, care being taken not to run in a further quantity before the carbon dioxide has escaped so far that frothing over is prevented. It follows, of course, that the soap-pan must be of much greater capacity

than is required for the same amount of soap made by the process described under (a), as ample space must be allowed for the tendency of the effervescing mass to rise rapidly. It is of the utmost necessity to keep the mass well boiling. Some operators even pass a current of air through the boiling mass in order to facilitate the escape of the carbon dioxide. This contrivance, however, cannot be recommended.

When all the carbon dioxide has practically escaped, the amount of sodium hydroxide required for the saponification of the neutral fat is introduced; the boiling is then continued, and the soap further treated in exactly the same manner as described above.

Having regard to the exaggerated statements that are made by interested parties as to the advantages resulting to the soap-maker by working with soap stock fatty acids instead of with natural oils and fats, the fact should be emphasised that soaps of the best quality are obtained only by boiling glycerides with sodium hydroxide, as described under (a).

With regard to the merits or demerits of the several soap stock fatty acids, it may be added that the 'autoclaved' material has a paler colour than the material obtained by the Twitchell process, but an inferior one to that made by the 'ferment' process. The loss of fatty material in the Twitchell process is practically *nil*, in the autoclave process it is very small, whilst in the case of the ferment process it is no longer negligible, a notable amount being lost in the middle layer. The soaps obtained from material prepared by the Twitchell process are the darkest. For this reason this process cannot be recommended for making 'genuine' soaps; it is essentially a process that produces material for low-class soaps. The most suitable material for making soap stock fatty acids by the autoclave process is that which is almost neutral, whilst raw material, high in free fatty acids, is better adapted for being worked up by the Twitchell process. Material rich in free fatty acids, especially in volatile acids, is not suitable for the 'ferment' process, which works best with good raw material (like the autoclave process). However, it must be pointed out that tallow and other high-melting fats are unsuitable for the 'ferment' process, and if these materials are required, they must be 'softened' by the admixture of low-melting fats, in order to become accessible to the action of the enzyme.

None of these processes has been able to displace the boiling of neutral glycerides; nor are they likely to do so in the near future. Although one or the other, or all of the three processes may be worked on a small scale, they are only employed for dealing with special material adapted to the making of special soaps, and those of inferior quality. Many installations erected for the production of soap stock fatty acids have been laid idle, within the author's experience, after practical results had demonstrated that first-class soap could not be obtained from such material.

(C) *Soap-making by Double Decomposition of Lime Soaps with Sodium Carbonate.*

The initial operations employed for the saponification of oils and fats have been

described under SAPONIFICATION (No. 1 'Saponification by means of lime in the open vat') as the modification worked out by Krebitz. The lime soap obtained is transported to the soapery, and introduced in small quantities into a soap-pan containing a 'boiling' solution of sodium carbonate. When the decomposition of the lime soap is nearly complete, a small quantity of sodium hydroxide solution is added. The soap-paste is next treated with salt, until the curd is thrown out. The contents of the soap-pan are then allowed to rest, when calcium carbonate settles out at the bottom of the pan as a heavy sludge, while soap curd separates on the top; a salt solution containing an excess of alkali forms an intermediate layer. The calcium carbonate sludge is drawn off, and, as it holds soap entangled (from 4 to 7 p.c.), it must be washed, and finally lixiviated with water in a filter press, to recover the occluded soap. The soap left in the pan after drawing off the spent lye is reboiled, and finished in the same manner as described above under (a).

This process is an extremely cumbersome one. The manifold operations prior to the soap-making proper, and the repeated washings of the sludge necessary to recover the entangled soap, entail manipulations which compare very unfavourably with the simplicity of the 'hot' process described under (a).

Several years ago (when prices of glycerin were high) the process was adopted by some small Continental soap-works, which up till then had run their spent lyes to waste. As the caustic lime exercises some purifying action in the case of low-class material (such as bone fat) containing proteins and gluey matter, this process may continue to be practised with low-class material, under certain favourable commercial conditions.

DIFFERENT QUALITIES OF HARD SOAPS.

The 'genuine' soaps are, with special reference to the process by which they are made, termed in technical parlance '*settled*' soaps.

Next in purity to the genuine soaps rank those soaps which are '*boiled on a lye*' and are termed 'curd' soaps. They are 'fitted' in such a manner that a somewhat open-grained soap 'curd' rests on a lye, which, in the case of the best class of soaps, consists of a salt solution containing only small amounts of sodium hydroxide or sodium carbonate. The water in these 'finished' soaps contains larger quantities of salt than is the case with genuine soaps, and, therefore, the percentage of fatty acids barely reaches 63 p.c. If the fatty raw materials and the lyes are pure a separation of dark soap (impurities) between lye and soap cannot take place; but if the fatty materials, &c., are somewhat impure, a small layer of dark soap separates between the 'curd' and the lye. This layer is left in the pan to be dealt with in a subsequent operation. If the fatty material used in the making of curd soaps is of somewhat low quality (kitchen grease, bone fat, &c.) it is necessary to finish on lyes somewhat strong in caustic alkali. The impurities, such as metallic soaps, &c., segregate on cooling in the form of veins in the soap, and cause the solidified soap to exhibit a slight 'marbling' or 'mottling.'

These soaps are, therefore, known as 'genuine mottled' soaps. The proportion of fatty acids in the soap is about 61 p.c.

A lower quality still than 'genuine mottled' soap is the type represented by the so-called 'Marseilles soap.' The Marseilles soap contains less than 60 p.c., as a rule not more than 57 p.c., of fatty acids. In order to give it sufficient hardness for handling, it must be 'pickled' in a brine solution. In the author's opinion a soap of this kind must be classed as a 'filled' soap. The manufacture of this soap is practically confined to Marseilles; and even there the demand for it is greatly diminishing.

The repute which this soap enjoyed led to the production of another kind of mottled soap, with which the Marseilles soap must not be confounded, and which, in the author's opinion, must be looked upon as an 'adulterated' soap. This imitation Marseilles soap, known as 'blue mottled' soap ('Eschweg soap,' 'Nantes soap'), is still a 'fitted' soap, inasmuch as its proportion of fatty acids is a definite one, lying between 46 and 48 p.c., and cannot be varied at will (as is the case with the soaps to be described below). This soap is made by 'filling' the genuine soap paste with solutions of sodium carbonate, sodium silicate, and (or) salt, which vary both in strength and in their several proportions according to the nature and composition of the fatty raw material used. This soap represents at the boiling temperature a mixture of two soap solutions, so carefully balanced by the art of the soap-maker that they have approximately the same specific gravity at a temperature slightly below the temperature at which the soap has been 'finished.' Hence, on solidification of the mass, no separation of the components into two distinct layers takes place. What separation does take place occurs so slowly that the solution which is richer in soap solidifies and imprisons the solution which is poorer in soap, before the latter has had time to segregate in the form of a lower layer. Hence, the desired 'marble' in the soap is obtained. The marbling is made more pronounced by the addition of ultramarine or 'copperas' for blue-mottled soap; by using other pigments, lamp black and 'English red,' grey mottled and red mottled soaps respectively, are produced. Such soap also requires 'pickling' before it is put on the market. The soap can be boiled direct from neutral fats in one operation, when, of course, the glycerin remains in the soap. But it is more profitable to the soap-maker to remove the bulk of the glycerin by saponifying the whole or part of the fatty material in a separate pan, thus obtaining a 'glycerin lye' and curd soap, which is then converted into mottled soap. The colour of the finished soap does not suffer thereby, whereas soap made from 'soap stock fatty acids' frequently becomes so seriously discoloured that it is practically unsaleable.

The lowest kind of 'fitted' soaps are those which are termed 'semi-boiled' soaps. These soaps are nothing but more or less concentrated saline solutions of soap, and can be made to contain any desired proportion of water. Some kind of purification is effected by allowing these soaps to drop a certain amount of 'nigre,' containing a good deal of the impurities in the

raw material; but, as a rule, these soaps are introduced into frames immediately after being made. The manufacture of these soaps may be considered as entirely obsolete, all the more so as the glycerin contained in the fatty raw material is lost, much as in the making of best soft soap from glycerides; indeed, these soaps may be likened to soft soaps. At present small quantities of this class of soap are still made in the south of Europe from low-class fatty material, rich in free fatty acids. This kind of soap must, of course, be considered an 'adulterated' soap.

In this country 'adulterated' soaps are mostly prepared by the aid of the mixing (crutching) machines into which 'neat' soap settled on a nigre is run, and is there incorporated with solutions of salt, sodium carbonate, and (or) sodium silicate to any desired extent, so that all grades of soap ranging from 60 p.c. of fatty acids downwards to even 10 p.c. can be, and are, made. In order to give those soaps sufficient firmness for handling they are either 'stoved' or 'pickled,' as the case may be.

In extenuation of the practice of 'filling' soaps with solutions of sodium borate, or of sodium carbonate or (and) silicate, is adduced the apologetic explanation that, besides hardening the soap, the added solutions possess detergent properties. The best that can be said for soaps of this class, which range in their proportion of fatty acids between 52 and 60 p.c., is that they might be considered as standing on the borderland between genuine soaps and 'adulterated' soaps. They should be openly described as 'filled' soaps.

There can, however, be no doubt that adulteration has taken place in the case of those 'filled' soaps which have been 'loaded' with weighting substances, such as clay, talc (sold as 'fillers'), chalk, barytes, asbestos, seed husks, &c., or with solutions of magnesium salts, &c. In the same category fall soaps filled with starch. In the opinion of the author soaps containing less than 50 p.c. of fatty acids should be looked upon as 'adulterated,' whether the 'filling' has detergent properties or not, unless the admixture be declared openly ('sand soaps').

Special kinds of soaps for toilet purposes are *remelted soaps*, *milled soaps*, and *transparent soaps*. For the manufacture of these the reader must be referred to Lewkowitsch, Chem. Techn.

Salts of lactic acid are not very suitable as emulsifiers or soap-substitutes, the former on account of their being easily salted out, and the latter because they are crystalline. Sulphonates of hydronaphthalenes and the corresponding anthracene and phenanthrene derivatives are recommended for addition to soaps to increase their lathering power, especially the potassium, sodium, and ammonium salts of tetralin-sulphonic acid. These can be added to the curd after its separation from the spent lye, or in the stamping-machines. Solid soaps do not become incrustated if not more than $7\frac{1}{2}$ p.c. of the sodium salt is added, and give a thicker lather. Ammonia soft soaps can be made from the ammonium salts. The optimum lathering power with soap powders is obtained with a 20 p.c. addition of the sodium salt. The same

proportion of the ammonium salt gives a sal-ammoniac and turpentine soap powder which gives off ammonia when dissolved in a little water. Almost all the commonly used filling materials in the soap industry are considered to be useless adulterants (W. Schrauth, *Seifensieder Zeit.* 1923, 30, 209-210, 223-224; *Chem. Zentr.* 1923, 94, iv. 160-161; *J. Soc. Chem. Ind.* Sept. 1923, vol. xlii. 897 B).

For the fine structure of some sodium salts of the fatty acids in soap curds, see S. H. Piper and E. N. Grindley, *J. Phys. Soc. London*, 1923, vol. xxxv. 269.

The discoloration that develops in time on the surface of soap made from maize oil is not due to the colour of the oil or to sunlight, but results entirely from atmospheric oxidation of the saponified unsaturated glycerides, e.g. sodium oleate and linolate. It is impossible to make a soap from ordinary maize oil that will remain white for any length of time when exposed to the air. Even when made in an atmosphere of nitrogen the resulting soap will in time turn brown in air. Overheating of the soap during manufacture greatly aggravates the defect. Dry soap, i.e. a well-grained soap or one that has been smoothed and then dried, does not become discoloured so quickly as a smoothed or moist soap. The more rapid deterioration of wet samples appears to be due to the sodium hydroxide set free by hydrolysis, which acts as a catalyst of the oxidation. The presence of sodium chloride appears to delay the development of colour, probably because it inhibits hydrolysis. Even first-class white commercial soaps made from maize oil will turn brown in a few hours when moistened and heated at 110°. If maize oil is very carefully heated in an inert atmosphere so that no local heating above 285° occurs, the resulting oil, if its iodine value has been reduced to 113 or less, will give a soap that resists oxidation and will remain white much longer than soap made from unheated oil.

Soap made with a weak lye (10° B., *d* 1.974) retains its whiteness much longer than that made with a lye of 18° B. (*d* 1.143) (E. G. R. Ardagh, J. C. Bell, F. S. Spence, and A. Murray, *Canadian Chem. and Met.* 1923, 7, 302; 1924, 8, 7; *J. Soc. Chem. Ind.* 1924, 43, B. 223).

2. Soft Soap—Potash Soap.

In the manufacture of soft soap the base used preponderantly is potassium hydroxide, small quantities only, if any, of sodium hydroxide being employed under certain conditions. Thus in summer it is the custom to saponify with a mixture of potassium hydroxide and sodium hydroxide, according to the desired consistence of the finished product. The manufacture of potash soap is much simpler than that of hard soaps, as it involves practically only one operation, viz. 'boiling' the glycerides with caustic alkali solutions in a pan, no 'salting out' being required. Hence the resulting product, after being properly 'fitted,' can be run straightaway from the boiling-pan into the vessels in which the soap is sold.

The method of manufacturing 'genuine' commercial soft soap for household purposes differs, however, essentially from that employed

in the manufacture of hard soap, in that the presence of potassium carbonate is required so as to produce a soap of clear translucent appearance which possesses the desired consistence for handling.

Soft soap used to be made in fire-heated pans; but during the present century these have been replaced in modern works by pans similar to those used in the manufacture of hard soap, and fitted with a 'close' steam coil in addition to an open steam coil or coils.

The fatty raw material, which for the best soap consists chiefly or preponderantly of linseed oil, is introduced into the soap-pan and churned up with steam, when a potassium hydroxide solution of about 20°Tw. is run in. While the saponification proceeds, lyes of higher strength can be used. When all the glycerides have been converted into soap, and the latter is just slightly alkaline, potassium carbonate solution is introduced. The soap will then contain an excess of water; this is removed by turning off the open steam and heating the mass with the aid of the close steam coil. At the same time the mass is agitated by a suitable mechanical arrangement so as to promote the rapid evaporation of the excess of water. By taking samples and examining their appearance and consistence on a glass plate, the operator is able to judge exactly the point at which the soap is 'finished.' The mass then represents practically a mixture of potassium salts of fatty acids with a solution containing all the glycerin from the fats, a slight excess of potassium hydroxide, and a certain amount of potassium carbonate. The two component parts of this mixture are so carefully balanced that, on cooling, a homogeneous mass is obtained which retains its transparency. If the soap is made from linseed oil only, the transparency will be retained even in winter, and the soap will not 'congeal'; but if the soap stock contains notable amounts of cotton seed oil, or even maize oil, and frost sets in, then the soap is liable to become dull ('blind'). Hence the choice of raw material is conditioned by the seasons. If some tallow is used in the stock, the harder potassium stearate or palmitate, or a mixture of both, crystallises out in star-like clusters, producing what is known in commerce as 'figging.' The same effect can also be obtained by replacing a portion of potassium hydroxide by its equivalent of sodium hydroxide.

In the soft soaps prepared in the manner described above all the glycerol is retained, and, as has been pointed out already, a certain excess of potassium hydroxide and notably of potassium carbonate, necessary in order to give the soap the inviting appearance the public demands.

By operating carefully, potash soaps can be made which are devoid of free alkali and potassium carbonate. Such soaps are, however, only manufactured for the purposes of the textile industry, or 'liquid' soaps for cosmetic purposes, when absence of free alkali or of carbonate is essential, and the appearance of the soap is of no importance. In this case it is indispensable to work with pure potassium hydroxide, as all impurities, such as sulphates, chlorides, and carbonates, pass into the finished soap.

The composition of a genuine potash soap

made from fats having the mean molecular weight 860 is, theoretically, as follows:—

Fatty anhydrides	38·700 p.c.
Combined potassium oxide, K ₂ O	6·843 „
Glycerol, water, and potassium carbonate (by difference)	54·457 „
	<hr/>
	100·000

Rosin is used for cheaper kinds of soft soap, just as in the case of hard soap. In the manufacture of soft soaps for textile purposes rosin must be avoided; and the presence of rosin in such a soft soap must be considered as distinctly lowering its value, or even as constituting adulteration.

Soft soaps, like hard soaps, are also 'filled' ('thinned out') with solutions of potassium silicate, potassium carbonate, potassium chloride, carragheen moss decoction, starch, and potato flour. The last two substances are largely used for the adulteration of opaque (white) soft soaps made on the Continent, especially the German 'silver soap,' in order to 'increase the yield.'

In the best soft soaps all the glycerol is retained, and its presence helps to impart to the soap the desired transparency. The endeavour to recover the glycerol has led to the production of soft soap from fatty acids (oleic acid and from 'soap stock fatty acids'). The production of soft soaps from these materials has gained ground, notably on the Continent. But the same strictures which have been made above with regard to hard soap made from such material may be repeated also in this case. High-class soft soaps, such as are in demand in this country, cannot be obtained with soap stock fatty acids. Whereas the fatty acids obtained by the Twitchell process are entirely unsuitable for soft soap, those made by the autoclave process can only be used for the inferior qualities. Slightly better than the soap stock fatty acids prepared by the autoclave process is the soap stock material obtained by the 'ferment' process. It should, however, be emphasised that such soaps are inferior to those made from glycerides. As the price of potassium carbonate is almost the same as that of potassium hydroxide, or slightly higher, it would be unremunerative to neutralise the free fatty acids in the soap stock fatty acids with carbonate, as is done in the case of hard soaps made from this material. There is, therefore, no inducement to use potassium carbonate in place of potassium hydroxide.

Commercial varieties of soap.—In order to suit various purposes, the variety of soaps that are being made is exceedingly great.

By far the largest quantities of hard soap are used for laundry, toilet, and other household purposes.

The most suitable soaps for laundries are either genuine mottled or 'settled' tallow-rosin soaps. The best class of *toilet* soaps contain, as a rule, 80 p.c. of fatty acids; but it must be understood that there are all varieties in commerce, down to the cheap transparent toilet soaps, which contain even less than 40 p.c. of fatty acids. Frequently medicaments, &c., are

incorporated and thus an enormous variety of *medicated soaps* is made.

Special objects are served by *floating soaps*, made by incorporating air with soaps while still in the pasty state; *disinfecting soaps*, containing carbolic acid, formaldehyde, &c.; *sand soaps*, which are made chiefly from finely-ground silica or infusorial earth, by mixing it with hard soap (and sometimes with sodium carbonate), so as to allow the mass to be shaped and handled like a soap cake.

During the last few years *shredded soaps*, made from genuine soap, and *ground soap*, also made from genuine soap, have come into use. These soaps may be considered as representing the best class of *dry soaps*. Usually, however, under the name of *dry soap* are understood those *washing powders* and *soap powders* which are prepared by grinding together hard soaps with sodium carbonate or sodium silicate, or both. Powdered Castile soap is said to be liable to occasional spontaneous ignition (Pharm. J. 1923, 314; see also J. O. Braithwaite, Pharm. J. 1923, 339). *Perborates*, *persulphates*, &c., have also been introduced into these soap powders under the plea that they add a bleaching effect to the washing effect.

Textile soaps are used in the textile industries, notably in the silk, woollen, and cotton industries, and form, as it were, a special group requiring brief consideration. In the silk industry the soap used for degumming the raw silk fibre is mostly made from olive oil or (chiefly in America) from lard oil. In the woollen industries soap is used (a) for scouring raw wool, (b) for scouring spun yarn, and (c) for scouring the woven woollen fabric; in the cotton industry it serves to remove 'stiffenings,' and is used for washing the dyed or printed fabric.

Special kinds of *textile soaps* are *dry cleaning soaps* (benzine soaps), *soap emulsions*, prepared by partly neutralising Turkey-red oil with caustic alkali (such soaps are now frequently mixed with carbon tetrachloride or chloroethylenes), '*softening*' ('cotton softener') consisting of a salve-like emulsion made by incorporating large quantities of water with genuine soap.

The facility with which foreign substances can be incorporated with, and are retained by, solidified, jellified, or liquid soap has led to the production of an enormous amount of all kinds of 'special' soaps, for each of which some valuable property (real or supposed) is claimed. It is quite impossible to give a classification of these, and it must, therefore, be left to the analyst to decide, in each individual case, whether a soap containing foreign substances must be considered to be an adulterated soap or not. Thus a soap sold as a sand soap is not adulterated soap. Nor would a soap containing *naphtha*, or *petroleum*, or *tar oils*, or *sulphur*, or *peroxides*, or *perborates*, &c., fall under this head, if sold as *naphtha soap*, *petroleum soap*, *tar soap*, &c. It should, however, be pointed out that, as a rule, these substances are very frequently accompanied by loading materials (especially sodium silicate solutions).

Valuation and analysis of soap.—In the valuation of soap, chemical analysis must play a prominent part, inasmuch as only thereby is it possible to ascertain the percentage of real

soap, the amount of other constituents, and the presence of foreign substances. Whilst chemical analysis will thus be resorted to in the first instance, it must not be forgotten that a host of other factors, such as appearance, consistence, lathering properties, &c., play an important part in enabling one to arrive at a definite opinion as to the value of a soap. Not every soap is suitable for a given purpose, and much depends, *ceteris paribus*, on the nature of the fat stock which has been employed.

In what follows the most trustworthy chemical methods applicable to the examination and valuation of commercial soaps, are described. No attempt is made to indicate a complete course of analysis embracing the search for all substances that may possibly be present, as such a course would be of little practical use.

Sampling of soap.—Great care must be exercised in sampling soap in order to avoid serious errors in the determination of water. On exposure to the air soap dries on the surface; and once a 'skin' is formed the outer portions of a cake protect to some extent the inner portions from loss of water by evaporation. In the case of hard soap, the sample for analysis should, therefore, be taken from the centre of the cake by cutting away all the outer portions; to what extent this must be done will be gathered by inspecting a transverse section, this showing to what depth drying has taken place. Such devices as taking a sample by means of a cork-borer, or by cutting a transverse slice from a cake, in order to obtain an 'average' sample, lead to erroneous results. If the sample under examination be a freshly made soap (containing about 30 p.c. of water), a fairly large portion should be weighed off rapidly, as the soap is apt to give up appreciable quantities of moisture to the dry atmosphere of the balance case. For the same reason the sample should not be sliced before weighing, except perhaps in the case of a milled toilet soap or of a thoroughly dried-out soap. The well-known contrivances for preventing loss of moisture during weighing must be resorted to, if highly-watered soaps be under examination.

(a) *Determination of Fatty Matter and of Total Alkali.*

Weigh off accurately 5–10 grms. of the sample (or 50 grms. on a balance sensitive to centigrams) and dissolve in hot water in a beaker or porcelain basin by heating gently; stir continually with a glass rod so as to prevent the soap from caking on to the bottom of the vessel. Add a few drops of methyl-orange and run in gradually hydrochloric, or dilute sulphuric acid (or dilute nitric acid if chlorides and sulphates are to be determined), until there is an excess of mineral acid. Heat, with constant stirring, until the separated fatty acids have melted into oily drops; add about 5 grms. (or 20 grms. for 50 grms. of soap) of dry beeswax, or paraffin wax, weighed accurately on a tared watch-glass (which is used afterwards for weighing the fatty matter), and heat again until the mixture of fatty matter and wax has collected on the top of the liquid as a clear transparent oily layer, free from specks. Rinse the glass rod with boiling water, heat until the fatty matter has

again collected into one mass, remove the vessel from the source of heat, and allow its contents to solidify by cooling. A white precipitate on the bottom of the beaker will indicate the presence of silicate or of 'fillings' insoluble in mineral acids.

The solidified cake is then detached from the vessel by means of a platinum spatula, lifted out of the liquid, rinsed with cold water, and placed on filter paper. Any small quantity of fatty substance adhering to the sides of the vessel is carefully scraped off and added to the cake. Dry the cake (by touching lightly with filter paper), place it on the watch-glass used before, bottom side upwards, allow it to dry in a desiccator and weigh it. (For the control of works' operations, when 50 grms. should be used, it is sufficiently accurate to weigh the cake immediately after drying with filter paper, taking care that no moisture remain in the cavities, if any, of the cake.) Should the cake contain any cavities (which only occurs when the fatty matter has not been heated properly) enclosing water, and perhaps even mineral acid, the fatty matter should be remelted in a basin over water, taken off after cooling, and dried as described above.

From the weight thus found the weight of the wax is deducted, and the difference returned as *fatty matter*. If no closer examination is made, it is, as a rule, returned as *fatty acids*. This is, however, only correct if the absence of neutral fat, wax, and unsaponifiable matter has been proved, *rosin acids* being looked upon as so much fatty acids, unless their separate determination is desired. With regard to the soluble fatty acids in soap, cf. Lewkowitsch, Chem. Techn.

It is a difficult matter to separate the fatty acids from soaps containing sodium silicate. In such cases it is best to dissolve the soap in alcohol, wash the insoluble residue with alcohol, evaporate the solution and washings, and to estimate the fatty acids in the residue of purified soap.

If, by subsequent examination, the soap is found to be free from neutral fat, wax, and unsaponifiable matter, the fatty matter is returned as *fatty acids*. In a complete soap analysis the fatty acids are calculated to anhydrides by multiplying their percentage number by 0.9675.

The replacement of potassium or sodium by ammonium in fatty soaps by means of ammonium chloride in aqueous solution and the ready dissociation of ammonium soaps when heated is used as a basis for a method of determining alkali in soaps. 3-5 grms. of soap are dissolved in 50 c.c. of hot water, 10 c.c. of 20 p.c. ammonium chloride solution added, and the mixture is steam-distilled for 1 hour in a Kjeldahl distillation apparatus, the vapours being passed into *N/2*-hydrochloric acid, the excess of which is afterwards titrated (F. L. Stüpel, Chem. Umschau, 1924, 31, 97; J. Soc. Chem. Ind. 1924, 43, B. 565).

The more fatty acids a sample contains, the more actual soap is present.

(b) Combined Alkali, Free Caustic Alkali, and Alkaline Salts.

The total alkali is the sum of the several amounts of alkali present in the soap as (1)

alkali combined with fatty (and rosin) acids, termed conveniently 'combined' alkali; (2) free caustic alkali; (3) alkali as carbonate, or (and) silicate, or (and) borate.

In case of hard soap the alkali is calculated to Na_2O , and in the case of soft soap to K_2O .

If a separate determination of sodium and potassium be required, the soap must be decomposed with hydrochloric acid, and the potassium in the acid liquid estimated as potassium platinic chloride.

(1) **Combined alkali** is usually found by difference, *i.e.* by subtracting the sum of the amounts of alkali obtained for (2) and (3) from the total alkali as determined above. It can, however, be found direct by titrating the alcoholic solution of the soap with normal acid, using methyl-orange as an indicator after neutrality has been established to phenolphthalein. This may be done as a check, or in order to dispense with the determination of the alkali present as carbonate, silicate, and borate (3), which obviously may then be found by difference.

(2) **Free caustic alkali.** A preliminary test is made by dropping an alcoholic solution of phenolphthalein on to a freshly-cut surface of the soap. Pink coloration indicates the presence of free sodium hydroxide (also of carbonate, silicate, and borate if the soap be moist). If the soap has dried out, the alkaline salts do not redden the phenolphthalein. In order to separate free caustic alkali from any alkaline salts, a portion of the sample is dissolved in absolute alcohol and filtered. The alkaline salts remain on the filter, so that the alcoholic filtrate may now be titrated, phenolphthalein being used as an indicator.

Free caustic alkali should be absent from well-made soaps, especially from toilet soaps. As a great deal of circumspection and experience is required so to 'fit' a soap that it contains practically no free alkali, most of the ordinary commercial soaps will be found to contain an excess of free alkali. If this be small, the free sodium hydroxide is mostly converted into carbonate on exposure to the atmosphere, so that in many cases no free alkali will be found, especially if only the outer portions of a cake be tested.

Free caustic alkali is determined quantitatively by dissolving 10-30 grms. of the sample in hot absolute alcohol in a flask, loosely corked in order to prevent absorption of moisture from the air. Highly-watered soaps must be first dehydrated to some extent, while access of carbon dioxide is excluded. The hot solution is filtered rapidly, care being taken that no soap-jelly separates out on the filter; if the operation is carried out judiciously, a hot-water funnel can be dispensed with. The filter is washed with absolute alcohol, and the filtrate received in a narrow-mouthed flask. Phenolphthalein is then added, and the solution titrated with decinormal hydrochloric acid. In some cases the alcoholic soap solution may exhibit an acid reaction to phenolphthalein. Acidity may be due to the soap containing an acid stearate (palmitate or oleate) owing to faulty 'fitting' or to fatty acid having been added to 'kill' an excess of alkali. The amount of decinormal alkali required to neutralise the solution is

calculated to free fatty acids, in terms of oleic acid.

(3) The precipitate left on the filter contains carbonate, silicate, and borate, with which other insoluble substances, added as 'fillers' (starch, talc), as also colouring matters, may be admixed. (With regard to the complete examination of this precipitate, *see* below.) To determine the alkali contained in the alkaline salts, the precipitate on the filter is washed with cold water, and the filtrate is titrated with standardised acid, methyl-orange being used as an indicator. The acid used is calculated to Na_2O .

(c) *Determination of Water.*

The direct determination of water in soaps is, as a rule, an unnecessary operation. In the case of genuine soaps it suffices for all practical purposes to calculate the fatty acids to anhydrides, and add their weight to the amounts of alkali in its various forms. The water is then found by difference.

The direct determination of water is, therefore, only resorted to in exceptional cases. The soap is cut into fine shavings, brought into a porcelain dish, and weighed with a glass rod, so that the skin which forms on drying and prevents the escape of water from the inner portions may be conveniently broken up from time to time. This is especially necessary in the case of highly-watered soaps.

It is then dried at 100° in an oven, or preferably at a lower temperature *in vacuo*, especially in the case of linseed oil soaps, which readily undergo oxidation. A method of estimating the amount of water by difference has been devised by Fitzpatrick (*Chem. News*, 1911, 104, 247). The soap is dissolved in absolute alcohol, the solution filtered, and the filtrate treated with anhydrous sodium sulphate and again filtered. The new filtrate is evaporated on the water-bath, and the residue dried in a steam oven. The water may be calculated from the weight of anhydrous soap and of substances insoluble in alcohol.

(d) *Examination of the Fatty Matter* ('Soap Stock').

If no wax has been employed in the separation of the fatty matter, the latter may be used direct for the following tests. Otherwise a fresh quantity of fatty matter must be prepared; the 'cuttings' are most conveniently used up for this purpose.

The fatty matter may contain besides fatty acids, (1) rosin acids, (2) neutral fat, (3) unsaponifiable matter.

(1) **Rosin acids.** Rosin acids are detected qualitatively by the Liebermann-Storch reaction. Their quantitative estimation (Twitchell's method) is based on the property aliphatic acids possess of being converted into their ethylic esters when acted upon by hydrochloric acid gas in their alcoholic solution, whereas colophony undergoes very little change under the same treatment. The analysis is carried out as follows:—

Two to three grms. of the mixed fatty and rosin acids are weighed off accurately in a flask, dissolved in ten times their volume of absolute

alcohol (with weaker alcohol the conversion of fatty acids into esters is not complete), and a current of dry hydrochloric acid gas passed through the solution, the flask being cooled by immersion in cold water. The gas is rapidly absorbed at first, and after about 45 mins., when unabsorbed gas is seen to escape, the operation is finished. To ensure complete esterification the flask is allowed to stand for an hour, during which time the ethylic esters and the rosin acids separate on the top as an oily layer. The contents of the flask are then diluted with five times their volume of water, and boiled until the aqueous solution has become clear. From this stage the analysis may be carried out either (a) volumetrically or (b) gravimetrically.

(a) *The volumetric method.*—The contents of the flask are transferred to a separating funnel, and the flask is rinsed out several times with ether. After vigorous shaking the acid layer is run off, and the remaining ethereal solutions, containing the ethylic esters and the rosin acids, washed with water until the last trace of hydrochloric acid is removed. 50 c.c. of alcohol are then added, and the solution is titrated with standard potassium or sodium hydroxide solution, phenolphthalein being used as an indicator. The rosin acids combine at once with the alkali, whereas the ethylic esters remain practically unchanged. Adopting 346 as the combining equivalent for rosin, the number of c.c. of normal alkali used multiplied by 0.346 will give the amount of rosin acids in the sample.

(b) *The gravimetric method.*—The contents of the flask are mixed with a little petroleum spirit, boiling below 80° , and transferred to a separating funnel, the flask being washed out with the same solvent. The petroleum spirit layer should measure about 50 c.c. After shaking, the acid solution is run off, and the petroleum layer washed once with water, and then treated in the funnel with 45 c.c. of a one-fifth normal solution of KOH and 5 c.c. of alcohol. The petroleum solution of the ethylic esters will then be found to float on the top, the rosin acids having been extracted by the dilute alkaline solution, with formation of rosin soap. The soap solution is then run off, decomposed with hydrochloric acid, and the separated rosin acids are collected as such, or preferably are dissolved in ether and isolated after evaporating the solvent. The residue, after drying and weighing, gives the amount of rosin acids in the sample.

A new method of determining rosins in soap has been based by Fortini (*Annali Chim. Appl.* 1918, 9, 102) upon the fact that rosin acids yield nitro-derivatives which are insoluble in petroleum spirit. 200 grms. of the mixed acids are dried for about 30 mins. at 100° in a current of carbon dioxide, and dissolved in 50 c.c. of petroleum spirit (b.p. 40° to 70°) in a separating funnel. The solution is treated with successive small quantities of 10 c.c. of nitric acid prepared by mixing 25 c.c. of fuming nitric acid (sp.gr. 1.52) with 75 c.c. of strong nitric acid (sp.gr. 1.48), and adding a few crystals of urea to destroy nitrous acid. The liquid is shaken for 2 to 3 mins. and allowed to stand until the two layers separate, when the acid layer is drawn off. The treatment is repeated with 5 c.c. of the nitric

acid, which is drawn off in turn, and the residual petroleum layer is washed first with ordinary nitric acid, and then with water, and filtered, the filtrate evaporated at a low temperature and the residue of fatty acids dried and weighed. The method is free from the drawback of Twitchell's method, which may indicate the presence of a small amount of rosin in pure fatty acids and thus necessitates a correction. It is also applicable to soaps containing rosins other than colophony.

(2) **Neutral fat.** A well-made soap will but rarely contain unsaponified fat. If neutral fatty substances have been added to the finished soap, as in the case of 'super-fatted' soaps (admixed with olive oil, &c., or, in the case of certain toilet soaps, with wool wax), they will be obtained together with any unsaponifiable matter present, and must be separated from it subsequently.

The neutral fat *plus* unsaponifiable matter is isolated in a direct manner from the sample of soap by dissolving a weighed quantity in water or alcohol, adding standard potassium hydroxide solution to neutralise free fatty acids (if any) phenolphthalein being the indicator, and exhausting the soap solution (see OILS, FIXED, AND FATS).

(3) **Unsaponifiable matter.** This is isolated and determined together with neutral fat. If no neutral fat has been found, the total ether residue consists of unsaponifiable matter. This is examined as described under *Examination of the unsaponifiable matter* under OILS, FIXED, AND FATS.

In addition to the substances mentioned, the presence of vaseline, paraffin oil, oil of turpentine, tar oils, naphthalene, petroleum hydrocarbons, hydrocarbons from 'distilled grease,' &c., may be suspected.

Examination of the fatty acids. The examination of the fatty acids themselves, after separation from rosin acids, neutral fat, oxidised acids (if any), and unsaponifiable matter (see OILS AND FATS), with a view to determining the nature of the 'stock,' is a complicated problem, requiring systematic application of the methods described in the article OILS AND FATS, under the heading *Examination of fatty acids*.

(e) *Substances insoluble in Alcohol.*

The determination of all those substances which are insoluble in alcohol is conveniently combined with the determination of free caustic alkali, by collecting the insoluble matter on a tared filter previously dried at 100°, and weighing after drying at 100°.

Good soaps yield but insignificant amounts of residue. Only transparent soaps manufactured by the 'alcohol process' will be found absolutely free from insoluble matter.

The residue obtained on the filter may consist of: (1) Water-soluble substances, such as chloride, sulphate, carbonate, silicate, or borate of the alkalis. (2) Mineral substances insoluble in water, viz. colouring matters and 'filling' and 'weighting' substances. (3) Organic substances, especially starch, dextrin, or gelatin (carrageen mucilage).

(1) **Water-soluble substances.** The residue on the filter is washed with cold water so as not to dissolve any gelatin that may be present.

Presence of silicate (if any) will have been noticed already in the determination of fatty matter when decomposing the soap by acid (see above under (a)). If the silica has not been estimated in the same portion in which the amount of fatty matter has been ascertained (provided no other water-insoluble substance be present), it can be determined at this stage by acidifying the filtrate with hydrochloric acid after the total alkali present in it has been determined by titration, and evaporating to dryness in the usual manner. The filtrate from the separated silica may be tested for boric acid. If boric acid be absent, the amount of carbonate *plus* silicate may be calculated from the alkali found by titration, the silica having been found direct by weighing. If boric acid be present and the proportion of borate be required, the water-soluble portion is best divided into three parts. In one portion the carbon dioxide is estimated, in a second portion the silica, and in the third the total alkali is determined by titration.

Chlorides and sulphates are best determined in aliquot portions of the acid liquor, obtained after separating off the fatty matter as described in (a). It should be remembered that in that case nitric acid must be employed for decomposing the soap.

(2) The portion insoluble in water is ignited, so as to burn off organic substances, and the residue is weighed. The ash is examined qualitatively and quantitatively in the usual manner.

(3) **Organic substances.** The microscopical examination of the total residue insoluble in alcohol may furnish useful indications. Thus starch will be detected; the microscopical examination may be corroborated by testing with iodine. If the quantitative determination of starch be required, the residue on the filter insoluble in alcohol is washed with cold water to remove water-soluble substances and dextrin, and boiled with dilute sulphuric acid, replacing the water as it boils away in order to convert the starch into dextrose. The liquid is then neutralised with barium carbonate, filtered, and the amount of dextrose estimated by titration with Fehling's solution in the usual manner. *Dextrin* has been washed out by cold water simultaneously with the soluble salts. The proportion of dextrin is estimated by precipitation with alcohol. This is best done in a small beaker, tared together with a glass rod. The liquid is stirred vigorously, so that all the dextrin is made to adhere to the sides of the beaker. The aqueous liquid is then poured off, the dextrin washed with alcohol, and its amount determined by weighing the beaker after drying at 100°. *Gelatin* is dissolved by washing the alcohol-insoluble residue with hot water. The filtrate should be tested with tannic acid to corroborate the presence of gelatin.

For the determination of other substances occurring in soap such as *glycerol, sugar, carbolic acid, alcohol, colouring matters, ethereal oils, &c.*, see Lewkowitsch, Chem. Techn. iii.

Castor-oil soap differs from other soaps in that a solution of the soap in water gives with phenolphthalein only a very slight pink colour, which does not become appreciably deeper on dilution. With the soaps of oleic, palmitic,

and stearic acids, and of oils and fats in which one or more of these acids predominate, the amount of acid required to bring about neutrality to phenolphthalein at dilutions of about 1 in 160 is approximately half the total combined alkali present. In the case of castor-oil soaps, however, the amount of acid required to produce neutrality at this dilution is very small, and not more than 3–11 p.c. of the total alkali. This difference in behaviour between castor-oil soap and other soaps offers another means of discriminating between castor oil and other oils. Mixtures of definite proportions of castor and arachis oils were prepared, saponified under standard conditions, an aliquot part of the soap obtained was dissolved in water at the correct dilution, phenolphthalein added, and the solution titrated with *N*/10 hydrochloric acid. From the results obtained the composition of the various mixtures was calculated; the maximum divergence of the calculated from the actual composition was 1.7 p.c.

Linseed and cotton-seed oils give lower results than olive oil for the percentage of the total alkali in the soap, which is titratable with acid before the neutral point to phenolphthalein is reached. Butter fat, coconut oil, and palm-kernel oil also give figures much lower than most other oils and fats, and there are appreciable differences between them. The lowest figure obtained for a fat other than castor oil was 19.2 for a sample of coconut oil. The samples of various grades of castor oil examined gave values varying between 3.6 (medicinal oil) and 7.9 (Madras) (H. B. Stocks, *Analyst*, 1923, 48, 590; *J. Soc. Chem. Ind.* 1924, 43, B. 102).

(2) SALTS OF THE ALKALINE EARTHS AND HEAVY METALS—WATER-INSOLUBLE SOAPS—METALLIC SOAPS.

A number of insoluble soaps of the individual fatty acids have been described in the section *Fatty acids* (see OILS, FIXED, AND FATS). These soaps are prepared by double decomposition of the alkali soaps with aqueous solutions of salts of the alkaline earths or metals, or by heating the free fatty acids with the oxides or carbonates of the metals.

These soaps are employed in the arts for the most varied purposes, extensive use being made of their property of dissolving, to a considerable extent, in petroleum spirit, naphtha, heavier petroleum hydrocarbons, coal-tar oils (carbolic acid), oil of turpentine, and fatty oils. Their solubility is increased by the presence of free fatty acids.

The most important soaps are—

Lead soaps (lead plaster) consisting chiefly of lead oleate.

Magnesium oleate, used in the process of dry-cleaning to prevent spontaneous ignition. **Aluminium soaps** enter into many compositions for waterproofing textile goods and papers, for preparing substitutes for leather, celluloid, india-rubber substitutes for insulating purposes, &c. Aluminium oleate is used especially as an 'oil thickener.' **Lead and manganese soaps** are used as 'driers' (*q.v.*) in the manufacture of boiled oils and varnishes. **Zinc, iron, nickel, cobalt, and chromium soaps** are employed in the manufacture of coloured varnishes, as also for water-

proofing leather and canvas, and to some extent as 'driers.' **Copper and mercury soaps** serve in the production of anti-fouling preparations, especially in the manufacture of paints for ship bottoms.

In this class of soaps must be also included the *metallic resins*, chiefly used as 'driers' (*q.v.*).

In the analytical examination the water-insoluble soaps are decomposed by means of a suitable mineral acid (hydrochloric, nitric, sulphuric), when the fatty acids are obtained as an oily layer; or, if the salts be decomposed under ether (which in many cases is the most advisable course), in ethereal solution, and the metal passes into the acid solution. Both the fatty acids and the acid liquor are then examined in the usual manner.

For the microscopic structure of soap, see Kenneth MacLennan, *J. Soc. Chem. Ind.* 1923, 42, 393 T.

For the determination of anhydrous soap in lubricating grease, see Joachim (*Ind. Eng. Chem.* 1924, 16, 725; *J. Soc. Chem. Ind.* 1924, 43, B. 661).

According to McBain, Harborne, and King (*J. Soc. Chem. Ind.* 1923, 42, 373), a method has been developed and standardised for the direct and rapid determination of the amount of finely-divided carbon which various soaps carry through filter-paper. This gives a 'carbon number' characteristic of each soap solution, which may be taken as a measure of the detergent action of the particular soap. The carbon number is defined as the number of grams of carbon carried through by 1 kg. of solution under standard conditions. The method of determination consists of the following: One grm. of 'Auk' carbon black is weighed to within 1 p.c., placed in a large test-tube containing 20 c.c. of soap solution, thoroughly shaken and placed in a thermostat for 23 hours, shaken again and kept for a further hour in the thermostat, and then poured on an 11.3 cm. No. 31 Whatman filter-paper. The filtration is carried out in the thermostat, and when about 10 c.c. of filtrate have been collected this is analysed and the amount of carbon determined. It is shown that by a slight variation of the conditions the detergent action of a soap may be enormously increased. There is an optimum concentration in moderate dilution for which the effect is a maximum; very slight addition of either acid or preferably alkali greatly enhances the detergent power. With rise of temperature the detergent power diminishes rapidly at first and then more slowly. There is surprisingly little difference between soaps as different as oleate and myristate (*Chem. Soc. Abstr.* 1924, 126, ii. 155). J. L.

SOAP-BARK and SOAP-ROOT. Soap-bark is the bark of a Chilean rosaceous tree, *Quillaja saponaria* (Mol.). The thin black dead bark has usually been almost or entirely removed from the commercial product, which consists mainly or exclusively of the heavy white layer of bast which glitters with crystals of calcium oxalate. This salt is mainly responsible for the large amount (13 p.c.) of ash present. The bark when shaken up with water yields a frothy solution, which is neutral in reaction, and is used in cleaning cloth when it is important to

preserve the original colours. The emulsifying substance is *saponin* (a collective name for a group of glucosides), which is not toxic, but is accompanied by two poisons, sapotoxin and quillajic acid. Saponin is widely distributed in flowering plants, and is usually associated with toxic substances. Its presence is familiar in a number of caryophyllaceous plants belonging to the genera *Saponaria*, *Gypsophila*, *Dianthus*, *Lychnis*, *Silene*, and others, whose underground parts are known as 'soap-roots.' The ordinary (red) soap-root is composed of underground stems and roots of the soap-wort, *Saponaria officinalis* (Linn.); the (white) soap-root of Hungary, Mediterranean countries, the Levant, and the East, is composed of the peeled roots of various species of *Gypsophila*.

When heated with dilute sulphuric acid gypsophila-saponin yields, in addition to sugars, *prosapogenin*, m.p. 207° (decomp.), crystallising in needles or prisms, $[\alpha]_D^{18} + 11.92^\circ$, forms a *semi-carbazone*, m.p. 241°, and is converted by 2 p.c. sulphuric acid into a *sapogenin* $C_{24}H_{34}O_5$, m.p. 267°–268°, crystalline rosettes, $[\alpha]_D^{18} + 90.86^\circ$ (Rosenthaler and Ström, Arch. Pharm. 1912, 250, 290–297; Chem. Soc. Abstr. 1912, i. 640). According to Karrer, Fioroni, Widmer and Lier, the sapogenin is $C_{28}H_{44}O_4$, and yields a methyl ether, m.p. 192°, a semicarbazone, m.p. 272°, and an acetyl derivative, m.p. 192°–194°. They name the substance *allosapogenin* (Helv. Chim. Acta, 1924, 7, 781–784; Chem. Soc. Abstr. 1924, i. 1091).

SOAPSTONE v. TALC.

It is reported that a large deposit of soapstone has been discovered at Zwettl in Austria, not far from the Bohemian frontier. The soapstone, which is stated to require very little preparation, can not only be cut, sawn, drilled, and polished, but will absorb many colours, a property that should lead to its extensive use in powder form in the colour industry. The deposit is the most important of its kind yet discovered in central Europe (J. Soc. Chem. Ind. 1923, 42, 934).

SOAP-WORT. *Saponaria officinalis* v. SOAP-BARK.

Although it is easily soluble in water, extraction of the saponin from soap-wort with boiling water only proceeds slowly, probably owing to adsorption by the large surface of the cellulose skeleton of the plant. The quantitative methods of determining the saponin content of the root by means of baryta, magnesia, and lead acetate give too low results or involve alteration of the saponin and consequent lowering of the hæmolytic index. In order to extract the saponin quantitatively and unchanged, the powdered root is exhaustively extracted with boiling water, the united extract evaporated to a syrup, and the saponin fractionally precipitated, first with alcohol and then with ether. The two precipitates obtained are each about 10 p.c. of the starting material, with an ash content of 10–19 p.c. and 4–6 p.c., and a hæmolytic index of 1:100,000, and 1:200,000 respectively. By means of the electrodialysis method of Pauli the ash in the saponin is reduced to 0.07 p.c. Elementary analysis of the alcohol and ether fractions gives, respectively, 47.88 p.c. C, 7.60 p.c. H, and

48.40 p.c. C, 7.21 p.c. H. On acetylation of the saponin acetyl derivatives of degradation products are obtained, from which a mol. wt. of 352 is deduced for the saponin. This, however, is much too low, and the behaviour of the substance on dialysis indicates rather a mol. wt. of 3000 or more. Commercial 'saponin pur. albiss' (Merck) has the same hæmolytic index (1:25,000) as the gypsophila root itself (L. Kofler and O. Dafert, Ber. Deut. pharm. Ges. 1923, 33, 215; J. Soc. Chem. Ind. 1924, 43, B. 73).

SOBREROL v. TERPENES.

SOD OIL v. DÉGRAS.

SODA (NATIVE) v. NATRON; TRONA. Also SODIUM SESQUICARBONATE, p. 193.

SODALITE. A rock-forming mineral of the composition $Na_4(AlCl)Al_2(SiO_4)_3$ and crystallising in the cubic system. Other members of this group of minerals are mentioned in the article LAPIS-LAZULI. It is white, grey, or bright blue in colour; sp.gr. 2.3; and occurs as a constituent of certain igneous rocks, especially sodalite-syenite. At Litchfield in Maine, on the Ice River in Kootenay Co., British Columbia, and at Bancroft in Hastings Co., Ontario, large masses of sky-blue to deep blue sodalite are found. At Bancroft it has been quarried in some quantity for use as an ornamental stone under the trade-names 'Princess Blue' and 'Alomite.' The material takes a good polish, and has somewhat the appearance of marble, but it is considerably harder ($H. = 5\frac{1}{2}$) than this. A green sodalite from Vesuvius, containing MoO_3 2.87 p.c., has been called molybdosodalite.

L. J. S.

SODAMIDE NH_2Na , prepared by the action of ammonia on the molten metal, m.p. 210° (Wöhler and Stang-Lund, Zeitsch. Elektrochem. 1918, 24, 261).

SODA-NITRE v. NITRATINE.

SODDITE, a radioactive mineral, of the composition $12UO, 5SiO_2, 14H_2O$, found in the Belgian Congo. Small dull yellow crystals, H. 3–4, D 4.627 at 17° (Schoep, Compt. rend. 174, 1922).

SODIUM. Sym. Na. At.wt. 23.00.

Atomic weight.—E. Moles and J. M. Clavera (Zeitsch. physikal. Chem. 1923, 107, 423) have converted sodium azide into sodium nitrate, and as the result of eight experiments the ratio $NaNO_3 : NaN_3$ is found to have a value which lies between the extreme values 1.30731 and 1.30738. From this the atomic weight of sodium is calculated to 22.998 ± 0.002 on the basis that nitrogen has the atomic weight 14.008. The present value is in full agreement with the value found by Richards and Wells (A. 1905, ii. 450) and all other modern determinations. The ratio $NaNO_3 : NaN_3$ confirms the value 14.008 accepted for the atomic weight of nitrogen. The present work confirms once more the statement that the atomic weights of carbon (12.005) and sulphur (32.060), derived on the basis $Na = 22.995$ by Richards and Hoover and adopted by the International Atomic Weight Commission since 1916, are incorrect. The values $C = 12.000$, $S = 32.070$ are to be preferred (Chem. Soc. Abstr. 1924, 126, ii. 174).

For sodium as a member of a radio-active series, see Brown (Chem. Soc. Abstr. 1913, ii. 8).

Occurrence.—Sodium is one of the commonest

and most widely disseminated elements, constituting about $2\frac{1}{2}$ p.c. of the solid crust of the earth. It occurs in nature combined with other elements in the following forms: sodium chloride, constituting the mineral *rock-salt* or *halite* of which very large deposits exist at Stassfurt in Germany, Northwich in Cheshire, Salzburg in Austria, and many other localities; sodium carbonate and chloride mineral in Kenya Colony, Walther (Amer. Min. 1922, 7, 86; Chem. Soc. Abstr. 1922, ii. 859); sodium nitrate or Chile saltpetre, forming deposits several feet thick in the rainless districts of northern Peru; sodium aluminium fluoride, Na_3AlF_6 , called *cryolite*, occurring in quantity locally in Greenland; sodium sulphate, *glauberite*, $\text{Na}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$, in small quantity; sodium sesquicarbonate, *trona*, $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$, in great quantities locally; sodium borate, *borax*, or *tincal*, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, in the beds of certain dried-up lakes; sodium compound silicates, among which are *albite*, soda-felspar $\text{NaAlSi}_3\text{O}_8$; *labradorite*; *oligoclase*; *sodalite*, $\text{Na}_4(\text{AlCl})\text{Al}_2(\text{SiO}_4)_3$; and *nepheline*,



all being rock-forming minerals occurring in vast masses; *analcime*, $\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$, and *natrolite*, $\text{Na}_2\text{Al}_2\text{Si}_3\text{O}_{10} \cdot 2\text{H}_2\text{O}$. Many rock-forming silicates which are not generally regarded as containing sodium as an essential constituent—as potash-felspar, lime-felspar, potash-mica, aluminium silicates and magnesium silicate—also contain varying amounts of sodium (see Dana, System of Mineralogy).

Sea-water contains about 2.6 p.c. of sodium chloride, and many mineral springs and certain lakes also hold a considerable amount of this substance in solution.

The atmosphere contains minute quantities of sodium salts, arising from the spray of the sea.

Plants also contain sodium salts, some in such amounts as to have served for the extraction of soda, others in small amounts only. From the plants sodium salts pass into all animal bodies. For the effects of sodium salts on the germination and growth of plants, see Blanck (Chem. Soc. Abstr. 1917, i. 624), Singh (Chem. Soc. Abstr. 1919, i. 374). For the distribution of sodium salts in plant and animal cells, see Funcoka (Chem. Soc. Abstr. 1920, i. 907). For the marine plants requiring sodium, see Osterhout (Chem. Soc. Abstr. 1913, i. 671).

The importance of sodium compounds was not so great as that of the potassium compounds until the Leblanc soda process was working on a large scale, and then the relative importance of the two sets of compounds was soon reversed. The predominating importance of the sodium compounds was greatly emphasised by the establishment of the Solvay soda process. The development of the present large-scale chemical manufacturing era began with the extension of the Leblanc soda process, and was augmented by the endeavours of that process to compete with the Solvay soda process, and hence the story of the growth of these two processes is of fundamental interest to practitioners of applied chemistry. The Great War of 1914–1918 further increased the importance of the sodium compounds, as the

German supply of potash salts from the Stassfurt district was stopped, and except where potassium salts are absolutely indispensable, the sodium salts may now be regarded as permanently established.

This article on sodium and its compounds is therefore necessarily long, and to facilitate quicker reference the derivatives are not arranged in groups as in a text book, but alphabetically.

Sodium acetate $\text{NaC}_2\text{H}_3\text{O}_2$. Historical, see this vol. under *Sodium Carbonate* (p. 159). Properties, see Vol. I. 26.

Sodium alloys. A large number of alloys of sodium with different metals have been prepared, the most important being those with potassium. These are liquid at the ordinary temperature and resemble mercury in appearance. They are produced either by melting the constituent metals together under rock-oil, or by fusing sodium with caustic potash (Jaubert, Ber. 1908, 41, 4116; Bull. Soc. chim. 1908, [iv.] 3, 1126). The alloy NaK_2 is now made commercially by fusing sodium with anhydrous caustic potash at a temperature of 350° . It oxidises rapidly on exposure to air, igniting spontaneously and yielding a mixture of the peroxides of sodium and potassium (which is used for the regeneration of deoxygenated air in life-saving apparatus). The liquid alloy has been used for high temperature thermometers in place of mercury.

Sodium aluminate $3\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3$. Properties, see Vol. I. 169. Preparation during manufacture of sodium carbonate, see p. 178, method 15; it is also used for making sodium thiosulphate, see p. 262, col. 1; and for making caustic soda, see p. 230, col. 1.

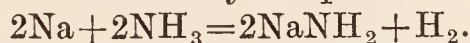
Sodium aluminate may be used as a Fire Proofing material. In order to impregnate fabrics with adherent hydrated alumina, they are soaked in a solution of sodium aluminate (sp.gr. 1.13), treated with carbon dioxide at 105°C . under a slight pressure, then washed and dried, or the aluminate may be decomposed by treatment with sodium bicarbonate. Another method is to moisten the alum-impregnated material with bicarbonate and then to treat with steam or with carbon dioxide at 100°C . (Pharm. J. 1924, 691); see also Goudriaan (Chem. Soc. Abstr. 1920, ii. 759).

Sodium amalgams are best prepared by adding successive small pieces of sodium to gently warmed mercury; as each piece dissolves it produces a flash of light and emits a hissing noise. After cooling, the amalgam with 1 p.c. sodium has an oily consistency, but with 1.25 p.c. sodium a pasty mass results, and with larger percentages of sodium hard crystalline amalgams are obtained. The fluid amalgams are only very slowly decomposed by water, forming caustic soda solution and hydrogen, but those containing a larger proportion of sodium react vigorously. The rate of decomposition is greatly accelerated by the addition of a small amount of zinc sulphate or lead acetate, which acts catalytically. By allowing an amalgam containing 3 p.c. of sodium to stand under water crystals of a compound NaHg_6 can be obtained (Kraut and Popp, Annalen, 1871, 159, 188), which at a temperature of 40° – 42° change into NaHg_5 (Kerp and Böttger, Zeitsch. anorg. Chem. 1900, 25, 1). Kurnakow

(*ibid.* 1900, 23, 439) and Schüller (*ibid.* 1904, 40, 385) have prepared and examined a number of sodium amalgams, many of which are definite chemical compounds. According to Schüller the compound of maximum m.p. (360°) possesses the formula NaHg_2 . If sodium amalgam be treated with solutions of the other alkalis or alkaline earths, partial replacement occurs, an amalgam of the metal employed being produced (Byers, J. Amer. Chem. Soc. 1908, 30, 1584; Böttger, J. pr. Chem. 3, 283). Sodium amalgam is employed in the laboratory as a reducing agent, and an amalgam containing 2-3 p.c. of sodium is used to some extent in gold extraction processes to prevent the 'sicken-ing' of the mercury by reducing the oxide of the base metals which collect on it and interfere with the proper working of the process.

Sodium amalgams are formed quantitatively when a solution of any sodium salt is electrolysed into a mercury cathode; this has been used as an analytical method, *see* Vol. I. pp. 309, 322, and it is the basis of several commercial methods of making sodium hydroxide (*see* p. 225).

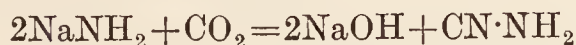
Sodium amide NaNH_2 or **Sodamide** was discovered by Gay Lussac and Thenard. It is produced when a solution of sodium in liquid ammonia (*see Sodium ammonia*, p. 157) is allowed to stand at the ordinary temperature:



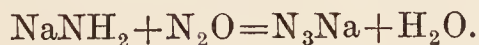
The reaction is considerably accelerated by the presence of a catalyst, such as platinised asbestos.

The usual method of preparation, and the one employed technically, consists in passing a stream of dry ammonia gas over metallic sodium heated to 300° – 400° in an iron retort, when it is obtained as a waxy mass which is white when perfectly pure, but usually possesses a brownish or greenish tint due to the presence of traces of other substances.

When heated, sodamide softens at 149° and melts at 155° , forming a bright green liquid. At a red heat it decomposes slowly into its elements, but it may be distilled under ordinary pressure at about 400° with only slight decomposition. On exposure to air it absorbs moisture and carbon dioxide and becomes converted into a mixture of sodium nitrite, carbonate and hydroxide. Sodamide is an exceedingly reactive substance; heated in a current of carbon dioxide it glows, and is converted into cyanamide:



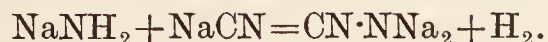
with nitrous oxide it yields sodium azide:



It is decomposed by water with explosive violence, producing ammonia and caustic soda, and acts as an extremely powerful dehydrating agent. On this account it has of late years been manufactured on the large scale for use in the artificial indigo industry to replace the caustic soda formerly employed to remove water in the conversion of phenylglycocoll into indigo blue (*vide* INDIGO, ARTIFICIAL).

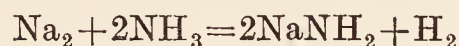
It has also found application in many other organic syntheses, and in the preparation of pure hydrazine, which it yields when heated with hydrazine hydrate.

Sodamide is an intermediate product in the manufacture of sodium cyanide. In this process, ammonia is led into a fused mixture of sodium cyanide, metallic sodium and carbon, when the sodamide first produced reacts with the cyanide to form disodiumcyanamide:



At a somewhat higher temperature, this compound is decomposed by the carbon present, being converted quantitatively into sodium cyanide.

Sodium ammonia. Sodium dissolves in liquid ammonia with the production of an intensely blue liquid. Ruff and Geisel have shown (Ber. 1906, 39, 828) that no definite chemical compound exists, and the liquid must be regarded merely as a solution of sodium in ammonia. The solution slowly decomposes on standing, with formation of sodamide—



(*see* p. 155).

When the deep blue liquid is evaporated it leaves a copper-red solid which has the composition NaNH_3 (Johannis, Compt. rend. 109, 900). The red solid easily loses ammonia and metallic sodium only remains.

Sodium analytical. The most characteristic analytical reaction furnished by sodium is the intense yellow colour imparted to the non-luminous flame of a Bunsen burner by all compounds of the metal. Viewed through a spectroscope two characteristic yellow bands of wave length 5896 and 5890, known as Fraunhofer's D-lines, are seen, and so delicate is this test that so small a quantity as 3×10^{-10} gm. of sodium can be detected by it. For the intensity of the D-lines, *see* Wood (Chem. Soc. Abstr. 1914, ii. 388). For the double spectrum of sodium, *see* Bancroft (Chem. Soc. Abstr. 1913, ii. 741). For the absorption spectrum, *see* Ladenburgh (Chem. Soc. Abstr. 1922, ii. 6), and Harrison (*ibid.* 1922, ii. 679). The arc spectra, *see* Eder (*ibid.* 1915, ii. 497), and Foote, Meggers and Mohler (*ibid.* 1922, ii. 598). The arc and spark spectra, *see* Seeliger and Thaer (*ibid.* 1921, ii. 566). The vacuum arc spectrum, *see* Strutt (*ibid.* 1919, ii. 485). The influence of the pressure of foreign gases on the spectrum, *see* Minkowski (*ibid.* 1922, ii. 242). For the fine structure of the band spectra of sodium, potassium and sodium-potassium vapours, *see* Smith (Proc. Roy. Soc. 1924, 106, No. A. 400). All the salts of sodium are soluble in water, so that no satisfactory precipitation reactions for its detection exist. The least soluble salts of sodium are the pyroantimoniate $\text{Na}_2\text{H}_2\text{Sb}_2\text{O}_7$, which requires 350 parts of cold water for solution, and the dihydroxytartrate. According to Ball (Chem. Soc. Trans. 1909, 2126) a solution of bismuth potassium nitrite containing caesium nitrite forms a reagent capable of detecting as little as 0.01 mg. sodium even in the presence of a considerable amount of potassium, a yellow precipitate being formed.

Sodium may be detected in presence of salts of potassium, magnesium, lead, zinc, aluminium, and the alkaline earths, if the solution contains so little as 50 mg. sodium per litre by adding magnesium acetate and uranyl acetate in the presence of 50 p.c. alcohol (Kolthoff, Pharm.

Weekblad, 1923, 60, 1251; and J. Soc. Chem. Ind. 1924, 43, B. 79). The precipitate is $3\text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{Mg}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{Na}(\text{C}_2\text{H}_3\text{O}_2) \cdot 9\text{H}_2\text{O}$. A. Blanchetière (Bull. Soc. Chim. 1923, 33, 807–818; J. Soc. Chem. Ind. Sept. 7, 1923, p. 868 A) has investigated the conditions under which this method gives the best results when testing small quantities of biological materials (blood, fæces, &c.), and finds that when filtering the precipitate on a Gooch crucible, pressure must not be applied until the precipitate has had at least five minutes to settle; 95 p.c. alcohol must be used for washing the precipitate—weaker alcohol dissolves it. For quantitative precipitation of the sodium, ten times the theoretical amount of the mixed acetate reagent is necessary. Phosphates must be removed before the determination is carried out or uranyl phosphate will be included in the precipitate.

Further details of the qualitative detection, see Vol. I. p. 240; of the quantitative estimation, see Vol. I. p. 248; and by electro-chemical analysis, see Vol. I. pp. 309, 322; and by volumetric alkalimetry, see Vol. I. p. 56.

Sodium arsenobenzol. The sodium salt of 3-diamino-4-dihydroxy-1-arsenobenzene. A bright yellow powder, very unstable in air, readily soluble in water, yielding an orange-yellow solution with an alkaline reaction. The solution gives no precipitate with caustic soda or sodium carbonate. With dilute hydrochloric acid it forms a precipitate which dissolves on addition of more acid. It gives a precipitate with picric acid, but no sulphur dioxide on heating (distinction from Neosalvarsan). Used in the treatment of syphilis and other spirochætal infections.

Sodium bicarbonate, see p. 181.

Sodium bromide, see p. 194.

Sodium carbonate Na_2CO_3 , and its hydrates $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ and $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$.

Sodium carbonate commercially and generally goes by the very old name 'Soda.'

In the history of applied commercial chemistry, the record of the methods employed to obtain these substances is second in importance only to that of the metallurgy of the old metals. Dr. Bakeland on this subject (Met. and Chem. Eng. 1914, 561), when referring to the Leblanc soda process, said, 'It will leave a treasure of information to science and chemical engineering, the value of which can hardly be over-estimated.'

The methods of preparation are chronologically arranged and each method is headed by the sodium compound used and the other reacting substance or substances, if any, and the chemical equation when possible. Under each method is found a brief description of the reaction, and then follows a chronologically arranged description of subsequent developments. For further details consult Lunge's *Sulphuric Acid and Alkali*, vols. ii. 1; ii. 2; and iii. As the number of methods is so great, ease of reference is obtained by consulting the following list and then turning to the page given.

Method 1. Natural soda, decomposed by heat, see p. 158, col. 2.

„ 2. Sodium salts of organic acids, decomposed by heat with or without air, see p. 159, col. 1.

Method 3. Sodium chloride, and potassium carbonate, see p. 159, col. 2.

„ 4. Sodium sulphate, and potassium carbonate, see p. 159, col. 2.

„ 5. Caustic soda, and carbon dioxide see p. 159, col. 2.

„ 6. Sodium sulphide, and a metal as iron and furnace gases, see p. 160, col. 1.

„ 7. Sodium sulphate, carbon and more or less furnace gases, see p. 160, col. 2.

„ 8. Sodium sulphide, and calcium carbonate (Leblanc's method), see p. 160, col. 2.

„ 9. Sodium silicate (solution), and carbon dioxide, see p. 175, col. 2.

„ 10. Sodium sulphide (solution), and carbon dioxide, see p. 175, col. 2.

„ 11. Sodium sulphate, and barium carbonate, see p. 175, col. 2.

„ 12. Sodium bicarbonate, and heat (Solvay's ammonia soda method), see p. 176, col. 1.

„ 13. Sodium nitrate, and potassium carbonate, see p. 178, col. 1.

„ 14. Sodium bicarbonate, and sodium sulphide, see p. 178, col. 1.

„ 15. Sodium aluminate, and carbon dioxide (Thomsen's method), see p. 178, col. 1.

„ 16. Sodium sulphide, iron oxide and coal, see p. 179, col. 1.

„ 17. Sodium sulphide, and barium carbonate, see p. 179, col. 1.

„ 18. Sodium sulphate, barium carbonate and carbon dioxide, see p. 179, col. 1.

„ 19. Sodium bichromate, and coal, see p. 179, col. 2.

„ 20. Sodium sulphate, and calcium bicarbonate, see p. 179, col. 2.

„ 21. Sodium sulphate, and carbon monoxide, see p. 179, col. 2.

„ 22. Sodium phenate, and carbon dioxide, see p. 179, col. 2.

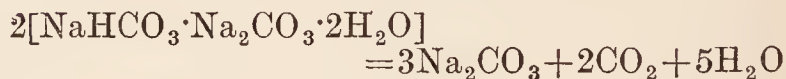
Then follow, pp. 179–181, descriptions of the properties and applications of the substances

1. Na_2CO_3 , 'soda ash.'

2. $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$, 'crystal carbonate.'

3. $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$, 'soda crystals.'

Method 1. Natural soda and heat,



This reaction occurs by heating to a little above 150° and leaves a nearly pure 'soda ash.'

Natural soda was probably first known in ancient times at Wady Atrein in Lower Egypt, and was then an article of trade and was utilised for washing, and soap and glass-making. Soda deposits are known in many parts of the world, and it is not impossible that in the future natural soda may become again the main source of the world's supply of soda.

Further particulars concerning natural soda will be found under *Sodium sesquicarbonate*.

The purification of the natural soda and its ignition is described by Naumann in Fisher's *Jahresb.* 1903, 304. The purified material is made into blocks and these are fired like bricks at 500° – 650° , whereby accompanying organic

substances are destroyed; the soda ash obtained contains an amount of insoluble matter, but otherwise it is almost pure. The natural soda from Lake Magadi in East Africa is calcined at a low red heat and yields a soda ash containing 99 p.c. Na_2CO_3 , and having a 'heavy' density very suitable for long transport.

Method 2. Sodium salts of organic acids, decomposed by heat with or without air, for example, sodium oxalate $\text{Na}_2\text{C}_2\text{O}_4 = \text{Na}_2\text{CO}_3 + \text{CO}$.—From the oldest times the ashes of certain plants growing on the sea-shore, and near salt springs and in the sea, have been prepared in quantity and used for making washing lyes, soap, and glass; the useful ingredient of the ashes being sodium carbonate.

In Scotland and Ireland the sea-weeds (fuci) were collected, dried and burned in pits dug in the sand or in heaps surrounded with loose stones, fresh quantities were added and the burning mass frequently stirred, till a semi-fluid mass was obtained which on cooling set into hard masses of a black or blueish colour, called 'kelp,' containing 2.5–5.0 p.c. of sodium carbonate.

In Normandy sea weeds were also burned. In the South of France land-shore plants, chiefly salsola, were burned and the ash was known as 'blanquette,' 'salicer,' 'soude douce.'

In Spain and principally at Alicant, and in the Levant, land-shore plants—salsola, atriplex, chenopodium, salicornia, kochia—were burnt and entered commerce as 'barilla' in the largest quantities, and were imported largely into France and England. In France the Napoleonic wars stopped the supply of barilla, and the soap, textiles and glass industries suffered accordingly, and Leblanc and others originated their alternative methods of obtaining soda.

In England barilla was the main source of soda until after the establishment of Leblanc's process in 1823.

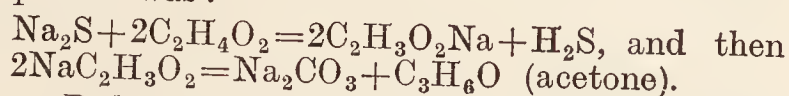
By lixiviation and decantation, the 2–30 p.c. of sodium carbonate was essentially extracted, and if the solution were not sufficiently pure, the impurities, sulphates, sulphides, and chlorides of sodium and of potassium were separated by evaporating the solution till the sodium carbonate would crystallise out as $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$. By boiling the barilla with water and lime a caustic lye was obtained, and the clarified lye of sodium hydrate was ready for the soap maker, either without or with previous concentration.

In the mother-liquors from the soda crystals from kelp in 1812 Courtois discovered iodine, and kelp became of more importance as a source of iodine than as a source of soda, but in the Glasgow process of extracting the iodine a salt known as 'kelp salt' was obtained that contained 8–10 p.c. sodium carbonate admixed with chloride and sulphates. Lunge, ii. 2, 77, 3rd ed. gives further particulars.

In 1736 Duhamel treated common salt with vitriol and prepared muriatic acid gas HCl , and salt cake Na_2SO_4 by Glauber's method of 1658; he mixed the salt cake with charcoal and heated to obtain a hepar or sulphuret Na_2S by Berthier's method; he treated the sulphuret with acid of vinegar, and so obtained a salt (sodium acetate) which he described, and he showed this when ignited gave an alkali which was different from the alkali of potashes, and

was identical with the mineral alkali obtained from barilla and by heating natural soda. This process of manufacturing artificial soda was patented by Duhamel.

In modern chemical formula Duhamel's process was:—



Duhamel's merit is not only that he first showed how to prepare mineral alkali artificially from common salt, and from salt cake, and from the hepar therefrom, but that he first showed the essential difference between mineral alkali (now called soda) and vegetable alkali (now called potash).

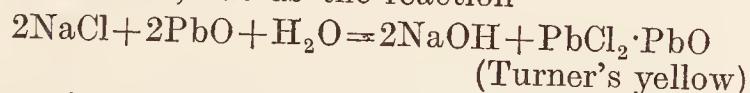
Modifications of Duhamel's method of preparing sodium acetate were used in Germany (Nicholson's Dictionary of Chemistry, 1808, article Soda), namely, precipitating solutions of sodium sulphate with either lead acetate or calcium acetate.

Method 3. Sodium chloride and potassium carbonate $2\text{NaCl} + \text{K}_2\text{CO}_3 = \text{Na}_2\text{CO}_3 + 2\text{KCl}$.—This reaction was employed by Bergmann when a mixed solution of the two reagents is concentrated by evaporation crystals of potassium chloride are obtained and then crystals of sodium carbonate ($\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$), or the whole mother-liquor may be evaporated to dryness. The process was described by Meyer in 1784. It was used by several manufacturers on the continent, and in this country was patented in 1795 by Lord Dundonald, and worked by Losh from 1802 to 1815 at Walker-on-Tyne.

Method 4. Sodium sulphate and potassium carbonate $\text{Na}_2\text{SO}_4 + \text{K}_2\text{CO}_3 = \text{Na}_2\text{CO}_3 + \text{K}_2\text{SO}_4$.—The salts were mixed in hot solutions, and by a complicated system of double crystallisation the potassium sulphate was removed in the two mother-liquors and in crystal pellicles deposited from the last solution at the temperature of the maximum solubility of Na_2CO_3 , viz. 35°. The soda crystals obtained were $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ (Accum, Nicholson's Dictionary of Chemistry, Soda, 1808).

Method 5. Caustic soda and carbon dioxide $2\text{NaOH} + \text{CO}_2 = \text{Na}_2\text{CO}_3$.

The key to this process was discovered by Scheele in 1773, viz. that brine treated with lead oxide was to a small extent converted into caustic soda, but as the reaction



occupied several days the atmospheric carbonic acid converted the caustic soda into mild soda, i.e. Na_2CO_3 , which after removal of the residual lead compounds could be separated from the great bulk of salt (95 p.c.) by crystallisation.

This process was used in England in 1782, and in France from about 1792; in 1806 it was being used by Losh at Walker-on-Tyne, and the crystal soda sold at £60 per ton.

In 1838 Watt and Tebbutt (patent 7538) boiled the ingredients instead of digesting in the cold.

In 1869 a modification was patented by Bachet (939 and 2401 of 1870) and was tested at Walker-on-Tyne, but as the product was then caustic soda it is described under *Sodium hydrate* (p. 227, col. 2).

Another method depending on the carbona-

tion of caustic soda solutions (p. 159, col. 2) was discovered in 1773 by Scheele, it was used by Proust, Pelletier and Deyeux, and the process was patented by Guyton-Morveau and Carny in 1782, and they worked the process at Croisic in Picardy, namely, moist piles of salt and slaked lime were left exposed to the air for some weeks, an efflorescence slowly formed and was carefully removed by hand—this was the soda. The process was conducted with considerable difficulty, and when the Revolution came and all processes for making soda had to be made public for the good of the state, Carney abandoned his process, and adopted Leblanc's process (p. 160, col. 2).

Caustic soda prepared by electrolysing a solution of brine in a diaphragm cell (*see under Sodium hydrate*, p. 225, col. 1) is always produced with a decreasing efficiency as the resulting solution of caustic soda increases in strength, and James Hargreaves and T. Bird described, in Eng. Pats. 18871 of 1892, and 5197 and 18173 of 1893, that by bringing a supply of crude carbonic acid (the exhaust from the gas engine) into the caustic soda compartment, so as to convert the caustic soda into sodium carbonate, the efficiency of the cell was made good again (Hargreaves, J. Soc. Chem. Ind. 1895, 1011), and this was explained by Hurter (J. Soc. Chem. Ind. 1897, 103–105) by reference to the migration velocities of the ions. The resulting liquor contains 10·9 p.c. Na_2CO_3 with up to 1 p.c. NaCl (Kershaw, Electricians, 1898, 547). The method of separating the salt is described by Hargreaves, Eng. Pat. 21178 of 1897. The sodium carbonate solution is generally converted into soda crystals $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ (*see Vol. II. 194*). The process has not been extensively used in this country, but in the U.S.A. there were three factories in 1919, *see J. Soc. Chem. Ind. 1920, R. 7*.

Method 6. Sodium sulphide and a metal as iron and furnace gases.

In 1778 Malherbe heated a mixture of sodium sulphate, and coal, with iron. The first reaction is the reduction of the sulphate to the sulphide, the next reaction is an imitation of the smelting of lead, copper and silver sulphides by heating the same with metallic iron to remove the sulphur as sulphide of iron; at this time the existence of metallic sodium was not known, so the course of the reaction could not then be understood, but doubtless what did happen was that sodium was liberated and then absorbing oxygen, moisture and carbonic acid from the furnace gases was converted into a mixture of sodium monoxide, sodium hydroxide and sodium carbonate. The melted product was cast into blocks, which on standing in the air absorbed moisture and carbon dioxide and fell to powder. The powder extracted with water gave a solution from which soda crystals were obtained without trouble. In 1779 this process was used for manufacturing purposes by Alban at Javel, Paris; Athenas also had a factory in Paris for this process (except that the sodium sulphate was prepared in a special manner and not by Glauber's process).

At a later date, 1828, the process was also used on the large scale by Siemens at Pyrmont, but with the addition of manganese dioxide along with the iron.

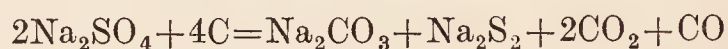
Malherbe's process above was modified by

Bryan Higgins in 1871 by replacing the iron by lead.

Method 7. Sodium sulphate, carbon and more or less furnace gases.

Sodium sulphate and carbon heated in more or less closed retorts were used about 1786 by De la Métherie to produce sodium carbonate and sulphur dioxide. The solidified salt was dissolved in water, and brought to crystallisation, and the impure sodium carbonate crystals were heated (with access of air) to remove accompanying sulphide and again crystallised. De la Métherie had to recognise that the amount of carbonate formed was small, while the main product was sodium sulphide, and as he could suggest no other way of removing the sodium sulphide than by treating the mixture with acetic acid, and after drying the sodium acetate igniting it, which was a repetition of Duhamel's process of 1736 (*see p. 159*), his process became a failure. But De la Métherie's failure was an advantage, in that it caused Leblanc to attempt to remove the sulphur, and this is dealt with in the next section, method 8.

The process was known about 1800 at Tennant's works. Berzelius and Graham approved the process; Gay-Lussac made large-scale experiments at Chauny; and Liebig in 1839, believing the reaction to be



and to take place at 300°C ., recommended it to Tennant's works as the best of all soda-making processes, and experiments on a large scale were made at St. Rollox.

Method 8. Sodium sulphide and calcium carbonate $\text{Na}_2\text{S} + \text{CaCO}_3 = \text{Na}_2\text{CO}_3 + \text{CaS}$.—This reaction was discovered in 1787 by Nicolas Leblanc. Having by Glauber's process prepared sodium sulphate from salt and sulphuric acid (and collected the by-product hydrochloric acid in ammoniacal liquor and converted the solution into sublimed ammonium chloride), and having strongly heated the sodium sulphate to remove the last portions of acid, Leblanc mixed the sodium sulphate with a quarter its weight of charcoal and half its weight of chalk, ground the whole and put into crucibles till two-thirds full, when they were covered but not luted. The crucibles were heated first gently, then until a paste formed, which was taken out of the crucibles. The mass containing sodium carbonate was either (1) powdered and boiled with water, the calcareous substance and unburnt charcoal settled and filtered off, and the solution boiled down and the separated soda dried in hot air; or (2) the mass was cooled, roughly crushed and allowed to fall to powder in the air and then washed as above.

Why Leblanc was led to add chalk to Métherie's mixture of sodium sulphate and carbon is not known, but it is probable that he was acquainted with the work of Margraf, who in 1750 formed a sulphuret of lime by heating gypsum with powdered coal and found it to be phosphorescent, and with the work of Canton in 1768, who also prepared a similar substance by heating oyster shells with sulphur.

On September 25, 1791, a patent was granted to Leblanc. It contained certain differences from his previous description, namely, no mention was made of the preparation of the sodium sulphate;

the proportions were altered to one of sodium sulphate, one-half of charcoal, and one of limestone or chalk; the mixture was spread out in a reverberatory furnace 6 ft. long by 4 ft. 2 ins. wide, with a very flat arch; during fusion the mass was frequently stirred with iron rakes; from the surface a large number of flames broke forth similar to the flame of a candle, and when these began to cease the batch was drawn out with iron rakes and collected in any kind of mould to give it the shape of the commercial blocks of soda (*i.e.* barilla, &c.). The above proportions have given the best results, but they might be changed: 100 lbs. of anhydrous sodium sulphate yields upwards of 150 lbs. of soda (that is the fused mass); no mention was made of the extraction of the sodium carbonate by solution or the removal of the insoluble matters. The soda was of higher strength than the soda of commerce (namely, barilla, &c.).

Leblanc borrowed from the Duke of Orleans £3000 in order to build soda works at St. Denis, Paris. The completed factory made five to six hundredweight of soda (*i.e.* black ash) per day and also some ammonia salt, and it prospered well, as Leblanc was the first to be able to compete easily with the price of Spanish barilla.

But in 1793 the Duke of Orleans was arrested by the Revolutionary Comité du salut public, his goods were confiscated, and among them was Leblanc's soda works. Leblanc's patent was cancelled in 1794, when the various ways of making soda were declared the property of the State in order to enable it to cast off dependence on foreign nations. Later Leblanc's patent was published and also an accurate description of the process, the furnaces and other apparatus and plans of the works. Leblanc claimed damages and did noble but honorary work for the State while other factories were being built, and worked his process, one by his previous competitor Carny (*see* p. 160, col. 1), and one even at St. Denis. The process was described in the *Ann. Chim.* 1797. In 1801 the ruined factory was returned to Leblanc, but he was without funds. 2900 francs were given him as a national recompense, a loan and an alms. In 1805 he learned that the indemnity of 52,473 francs due to him was already covered by the previous reconveyance of the works, and being then without hope, in 1806 he shot himself ('Nicolas Leblanc: sa vie et ses travaux,' by Aug. Anastasi, Paris, 1884).

Soda works were soon founded in Paris, Rouen, Chauny, St. Gobain for glass making, Alais, Marseilles for soap making, and at Thann for making textiles.

In 1814 the process was started in England on a very small scale at Walker-on-Tyne by Losh; in 1818 at St. Rollox by Tennant's works; in 1823 at Liverpool on a really large scale by James Muspratt, who so improved the process that the product instead of containing 17–20 p.c. sodium carbonate, as did the product of other French and English makers, was made to contain 41 p.c. sodium carbonate (E. K. Muspratt, *J. Soc. Chem. Ind.* 1886, 408). But the escape in Liverpool of hydrochloric acid gas in preparing the sodium sulphate from salt and sulphuric acid was beyond endurance; the locality rose in protest and the Corporation

compelled the removal of the works. (Details of the later methods of condensing this hydrochloric acid gas, and the uses to which the liquid acid were put, also methods of utilising the hydrochloric acid gas as such will be found in the second volume under the heading CHLORINE.)

When the artificial ash was exported or was kept before use it was found that it lost strength considerably, and this led in 1830 to the extraction of the sodium carbonate, by lixiviation, evaporation of the liquor, and calcination of the residue without or with sawdust, according as to whether the accompanying caustic soda was advantageous or objectionable, and the commercial product then became 'white ash,' which was either 'caustic ash' or 'carbonated ash,' according to the amount of accompanying caustic soda.

The next stage in making a purer alkali was the manufacture on the largest scale of 'soda crystals' ($\text{Na}_2\text{CO}_3 + 10\text{H}_2\text{O}$) by dissolving carbonated white ash in water, settling out the small amount of insoluble matter and cooling to crystallisation; from black ash direct these crystals could only be made of sufficient purity with the greatest difficulties.

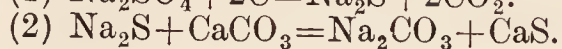
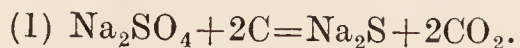
From 1830 the number of Leblanc alkali works increased rapidly, principally around Widnes, St. Helens, Runcorn, Manchester, Newcastle-on-Tyne, Glasgow, and Birmingham. In Germany the first works was built near Magdeburg about 1843, then near Cassel, and later at Aachen and in the Rhine districts. In Austria the first works was erected in 1851 in Moravia, then in Silesia, and very large works in Aussig.

But though the process was well established by 1830, yet scientific explanation of the reaction was incomplete.

The first difficulty in understanding the rationale of the process lay in the general belief that calcium sulphide is soluble in water; and therefore Thenard assumed that alkali makers' waste was not essentially calcium sulphide but a basic sulphide. Dumas in 1830 (*Traité de Chimie*, 11, 474), judging from the proportions of the materials used, considered that the basic sulphide was $2\text{CaS} \cdot \text{CaO}$, and this view was accepted almost without question for a long time. Kynaston, in 1858, suggested that a compound of CaS and CaCO_3 existed. In 1861 Gossage, in a *History of the Soda Manufacture*, showed that CaS prepared from calcium sulphate and coal (Margraf, 1750) is quite insoluble in water. In 1863 Scheurer-Kestner (*Compt. rend.* 57, 1013) found that the solubility of CaS in water at 12.6°C . is only 1 in 12,500 parts of water, and that it is slowly decomposed by a solution of Na_2CO_3 into Na_2S and CaCO_3 . Thereafter it was recognised that alkali makers' waste contained its sulphur in the form of CaS .

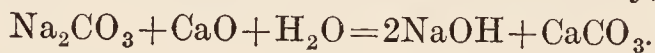
A second difficulty arose as to the mode in which the carbon burnt. Dumas, judging from the proportions of the ingredients, assumed carbon monoxide to be formed, but Unger (1847–8) showed that carbon dioxide was almost the only product, and Scheurer-Kestner (1862) and Kolb (1866) confirmed that the first stage of the reaction is $\text{Na}_2\text{SO}_4 + 2\text{C} = \text{Na}_2\text{S} + 2\text{CO}_2$. The conversion of the sodium sulphide into carbonate was shown by Scheurer-Kestner

(1865, Compt. rend. 64, 615) to occur at the moment when the Na_2S fused and penetrated the chalk. The reactions are therefore



These essential reactions are accompanied by several secondary reactions, which will now be referred to.

During the roasting the mass is of course unequally heated and some parts reach an unduly high temperature; this high temperature is experienced principally towards the end of the operation, and then it has been shown by Kolb and by Scheurer-Kestner that the limestone decomposes with the coal $\text{CaCO}_3 + \text{C} = \text{CaO} + 2\text{CO}$, and the carbon monoxide, as it escapes from the blowholes in the pasty mass, burns like a number of candle flames tinged yellow by sodium vapours, and this characteristic appearance is accepted as a sign of the completion of the operation. The quicklime thus generated causes a secondary reaction to occur when the sodium carbonate is extracted from the black ash by lixiviating it in warm water, namely,



This secondary reaction was in the first instance a disadvantage, in that the sodium carbonate solution contained a smaller or larger proportion of caustic soda, to remove which the solution had to be admixed with sawdust, evaporated to dryness, and ignited to obtain a soda ash free from caustic soda; then followed, 1853, Gossage's method of fishing the crystal soda $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ as it separated from the boiling solution, so as to obtain a purer carbonate, and the mother-liquor, 'red liquor,' was (1) evaporated to obtain an impure carbonate containing much caustic soda, 'caustic ash,' or (2) after oxidising the accompanying small quantity of sulphides by nitre, the evaporation and fishing out of the 'crystal soda' was continued, until he obtained the caustic soda comparatively pure as 'cream caustic' $\text{NaOH} \cdot \text{H}_2\text{O}$. The manufacture of caustic soda, at first quite foreign to the Leblanc soda process, became of increasing importance, and when the Solvay ammonia soda process developed so that it could compete and more than compete in the manufacture of soda ash, then the Leblanc soda works, by increasing the lime in the black ash mixing, increased the proportion of caustic soda produced, and still later by causticising the black ash liquor produced essentially only caustic soda and almost ceased to be 'soda' works in the original sense of the word soda, that is, Na_2CO_3 . Further details on this will be found under the heading *Sodium Hydroxide*, p. 214, col. 1, to p. 220.

During the lixiviation of the black ash the strong sodium carbonate solution reacts slowly on the calcium sulphide to form again sodium sulphide and calcium carbonate; in the cold this reversed reaction amounts in 48 hours to 2.1 p.c., but in the boiling solution it amounts in 4 hours to 3.7 p.c. (Kolb). This reaction and the imperfect mixing of ingredients for the black ash, or the imperfect stirring of the black ash cause the black ash liquor to contain sodium sulphide, and many methods have been used for destroying this, bubbling air or carbonic acid through, adding

zinc oxide, ignition in the air, or ignition with nitre. The action of the atmospheric oxygen on the sulphide produces another impurity, namely, sodium thiosulphate.

The impurities accompanying the ingredients of the black ash, namely, iron, silica, alumina, combined nitrogen, phosphates, fluorides, chlorides, introduce into the black ash solution iron-sodium sulphide, sodium silicate, sodium aluminate, sodium cyanide, sodium sulphocyanate, sodium ferrocyanide, sodium phosphate, sodium fluoridophosphate, and sodium chloride.

Further details of the old method of making sodium carbonate by the Leblanc process are next given, because, as far as the making and dissolving of the black ash, the method is almost the same as when making sodium hydrate, and because of the importance of the whole process in the past and of its bearing upon technological chemical development.

Raw Materials.

Sodium sulphate (salt-cake).—This is nearly always obtained by the decomposition of common salt by sulphuric acid, or else by Hargreaves and Robinson's direct process from common salt, pyrites kiln gases, and air (*cf. Sodium sulphate*, p. 250, col. 1, to p. 256).

It should be a white or yellowish powder containing only porous, friable lumps, and no fluxed pieces which nearly always inclose some raw salt and decompose badly in the black-ash furnace. Good, strong soda cannot be made with salt-cake containing more than 0.5 p.c. of undecomposed NaCl . Good commercial salt-cake contains 96–97 p.c. of Na_2SO_4 .

Calcium carbonate.—Both limestone and chalk are employed—and the purer the better. Magnesian limestone cannot be used. Limestone or chalk containing much silica causes a great loss of soda in the insoluble state. The chalk ought to be dried. Either material ought to be crushed to about 2-in. cubes. The Tyneside works mostly use the chalk brought down from the Medway by colliers as ballast. The Lancashire works employ mostly Buxton limestone, which requires less stirring in the furnaces than chalk, and requires less heat for the 'balling' process. In most cases the lime mud obtained in causticising the liquors by lime is used to replace part of the limestone in the black-ash mixture.

Coal.—The quality of the coal employed for the black-ash mixture is of great importance. It ought to contain as little ash as possible, and this is difficult to obtain in the small coal or 'slack' used; lump coal is much purer, but it is too dear for this purpose. Even after washing, small coal rarely contains less than 5 p.c. of ash; 6 p.c. is the maximum tolerated by some German alkali works; but in England 'slack' containing 8 p.c. ash is considered as very good for mixing. The coal ashes, consisting principally of aluminium and calcium silicates and ferric oxide, cause the formation of insoluble double silicates, which withdraw a considerable portion of soda in a non-available form. The more ashes the mixing-coal contains, the less soda ash will be obtained with it. Good lignite or crushed coke, if otherwise pure, can be well employed in

mixing. In any case care must be taken to decide by preliminary trials on a working scale whether a certain description of coal will answer for soda-making or not, as the whole success of the operation depends upon this, and analyses cannot entirely decide this point beforehand.

The nitrogen contained in coal, which varies from 0.5 to 0.75 p.c., gives rise to the formation of cyanides, part of which are converted into cyanate by the oxidising action of the flame. The moisture of the air decomposes the cyanate, with formation of ammonia, which is evolved during the cooling of the balls. But another portion of the cyanide remains behind, and is, during the lixiviation, converted into ferro-cyanide.

J. Pattinson (in Trans. Newcastle Chem. Soc. 4, 183) gives analyses of nine descriptions of mixing-coal as used on the Tyne. That described as 'good' contains, in 100 parts, 61.19–66.45 fixed carbon, 25.27–27.35 bituminous substances, 0.6–1.47 volatile sulphur, 0.1–0.3 sulphur in ashes, 4.8–8.32 ashes, and 1.01–1.67 moisture. 'Inferior' mixing-coal contains only 56–58.8 fixed carbon, and 12.56–14.22 ashes.

Mixing-coal acts all the better the more finely divided it is; it is, however, rarely ground by itself, especially as it is mostly employed in the state of 'small' or 'slack,' but is only screened and roughly mixed with the other materials.

In order to fully decompose the sodium sulphate, an excess of calcium carbonate and coal is always employed. Taking an average of the many mixtures employed in practice, we may assume that with 100 parts of pure Na_2SO_4 usually about 100 parts of pure CaCO_3 and 35 of pure C are employed—that is, to 1 molecule of Na_2SO_4 1.42 mols. of CaCO_3 and $4\frac{3}{4}$ mols. of C; or, say, $1\frac{1}{2}$ of CaCO_3 and $4\frac{3}{4}$ of C. In a case like the black-ash process, where the mixture never enters into complete fusion and the ingredients are never absolutely mixed with one another, the decomposition of the most valuable portion, the Na_2SO_4 , can be brought about only by a mechanical excess of the other ingredients, which ensures that every portion of the Na_2SO_4 comes into contact with them.

In order to lixivate the resultant black ash, it must have a certain degree of porosity, and must, moreover, be further disintegrated during the treatment with water. Without this, the lixiviation would require too much time, too high a temperature, and too great dilution of the liquor, and would thus produce a very inferior liquor, as well as a bad yield of soda. The above condition is practically attained by employing an excess of limestone and coal, which in the last stage of the process, when the temperature is at its highest, and the mass has become pasty, react (p. 164), and the carbon monoxide causes it to become honeycombed, like the dough in a fermenting loaf of bread. The caustic lime remains behind, and during the lixiviation becomes hydrated and causes the balls to swell and to burst. A further excess of limestone and coal, which ought not to be too great, produces greater porosity of the black ash in a purely mechanical way, since they are not

fused like the remainder of the mass. Lastly, some portion of the coal is unavoidably burned before it can enter into action. All these reasons fully explain the necessity of employing an excess of limestone and coal.

Black-ash Furnaces.

Black ash was made first in this country in reverberatory furnaces in which the mass was stirred by strong men with long and heavy slices and rakes, and though these tools are no longer used, yet as a matter of historical interest, the following illustrations (Figs. 1, 2, and 3) and description are added. The furnaces were substantially built and well-braced, and the position of the working doors and shape of the furnace allowed easy access for the working tools to all parts of the beds.

Fig. 1 is a sectional plan along line AB of Fig. 2, passing through the hollow fire-bridge, but showing the beds and the pan from the top; Fig. 2 is a sectional elevation along line CD of the plan; Fig. 3 is a front elevation, showing only the firing hole and the drainer in section. Such a furnace worked off a 3-cwt. charge of salt-cake in 45–50 mins., so that with the necessary pauses for cleaning the fire, &c., 24–27 balls were made daily. On the extreme left of each figure the fireplace is seen, it is provided with wrought-iron grate-bars; the bar *b* assists in poking up the fire from below from the fire-cave *c*. (Such 'cave-fires' were said to consume less coals than fireplaces with their ash-pits at the level of the floor, by the greater facility they offer for attending to the fire.) At *d* the fireplace is stepped backwards, so that the flame ranges all over the bridge *e*. The latter was very carefully and strongly built of the best fire-bricks procurable, and lasted about 3 months. It was $2\frac{1}{2}$ – $3\frac{1}{4}$ ft. from front to back, and usually built hollow. A cast-iron bridge plate, $1\frac{1}{2}$ –2 ins. thick, prevented the charge from fluxing through the bridge; it was protected against overheating by an air channel, open at each end. *h* and *i* are the two furnace-beds. The charge was put through a hopper *k* or else through the door, on to the back bed *i*, which was 3 ins. higher than the front bed *h*; to this the charge was transferred, when it was empty, in order to be finished and drawn out through its door. Sometimes three-bedded furnaces were met with. The front bed *h* was made of bricks on end, and was set upon a layer of ground chalk or fire-clay, to isolate it from the foundation. The bricks were set dry, as closely together as possible (preferably grinding them upon one another, so as to minimise the width of the joints), and were grouted on the top with a thin paste of fireclay. The long joints were made to run towards the door, and the whole bed was made to slope about 2 ins. that way, in order to facilitate the working of the tools. The back bed *i* was made of bricks on edge (i.e. $4\frac{1}{2}$ ins. high). The diagram shows how these beds were made within fire-brick 9-in. walls, so shaped that the tools could easily reach every part of the beds, and leave no dead corners. The front or working-bed, even if made of the best material and with the greatest care, rarely lasted longer than 5 months.

On the Tyne the furnaces were entirely cased in cast-iron plates, tied together by upright binders and tie-rods; but in Lancashire the plates were frequently replaced by the less substantial plan of simple straps of wrought iron, 3-6 ins. broad and $\frac{3}{8}$ in. thick.

In front of the working-doors there were special door plates and supporting bars for the tools. The doors were best closed by fire-clay slabs, surrounded by an iron frame, and hung from a standard with chain, pulley, and balance-weight.

The large quantity of waste heat in the gases from these furnaces was utilised in the evaporating pans situated on the right-hand of all three figures, as described later on under the head evaporating to monohydrate, p. 171, col. 2, last par.

The work in the black-ash furnace was carried on as follows: The mixture was put on the back bed, where it was levelled, and during its stay there was twice turned over, in order to dry it and heat it. When the charge in the front bed had been drawn out the fire was allowed

FIG. 1.

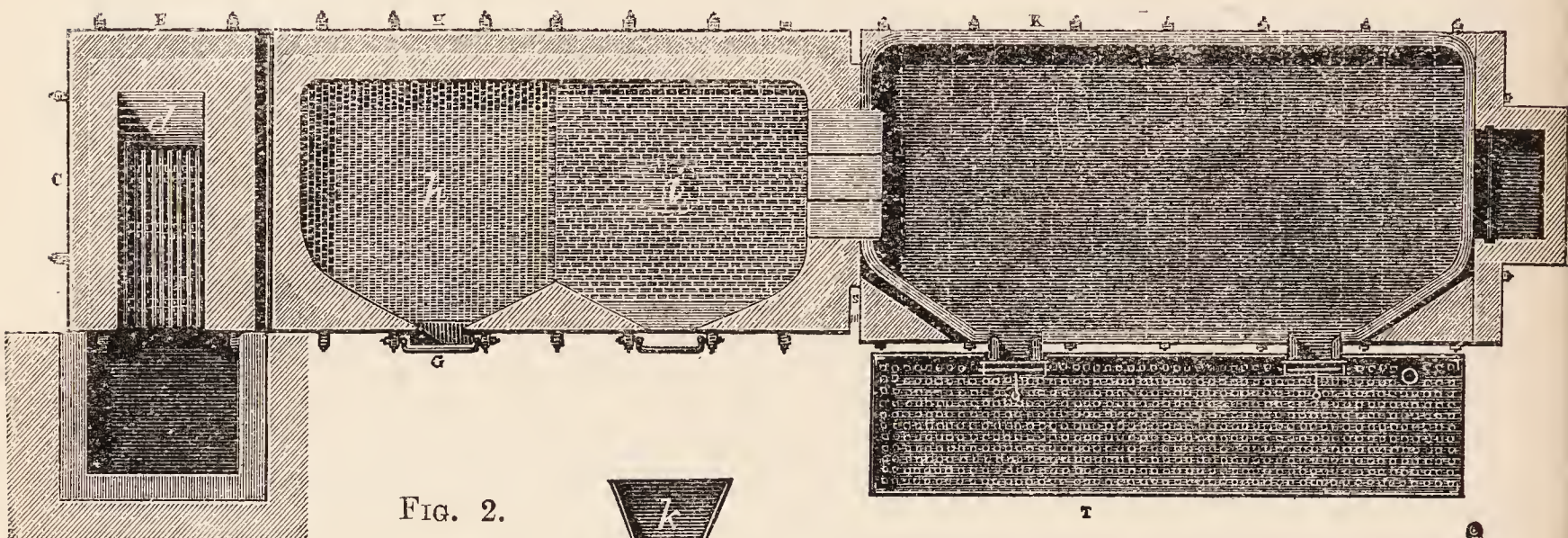


FIG. 2.

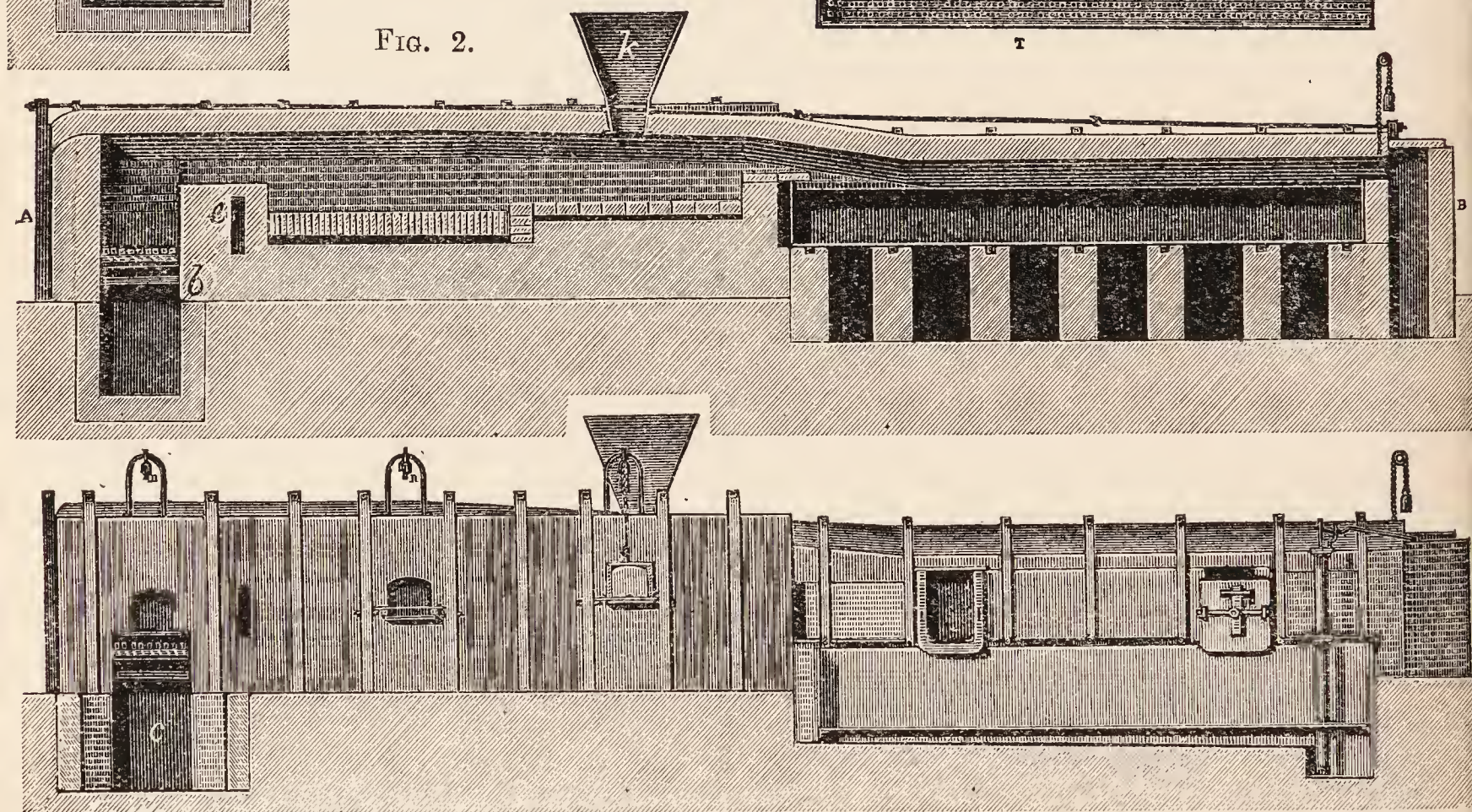


FIG. 3.

to play on the empty bed for a little while to make it hot, and then the previously heated charge was pushed over from the back bed. Sometimes a portion of the charge was left a little longer on the back bed ('splitting a ball'). As soon as the back bed was empty a fresh charge was put in. The principal work, of course, was on the front bed, which was heated to at least the melting-point of silver.

The watchfulness, strength and endurance required from the furnace men were very great, and as it was very easy for them to turn out good or bad black ash, they were paid by some method both for the quantity and quality of

their work. The time required for a batch was about 1 hour. At the end the mass stiffens and the evolved gases escaping only with difficulty cause the mass to swell up like a fermenting loaf of bread, and a number of pointed flames of CO coloured intensely yellow by sodium vapours squirt from the surface. The pasty mass was lastly raked out from the furnace into an iron bogie to cool.

The yield of black ash is about $1\frac{3}{4}$ times the weight of the salt-cake furnaced. Properly made black ash has a blackish-brown, in some places a liver-brown, surface; on breaking,

it exhibits a slate-grey colour and porous, almost pumice-like, structure, and looks homogeneous, without any black or white streaks or lumps. Balls which are quite black on the outside are made with too much coal, or are very badly wrought, so that the mixing coal was not all consumed and the ball could not be 'cleared.' If there was a deficiency of limestone, or if the balls were over-heated,

they are very dense, with pale pink spots outside, and on breaking their colour is pink or purple, in the worst case brick-red. Such black ash contains very much sodium sulphide or even polysulphide. Kolb found this to occur whenever the melting-point of silver was exceeded. 'Soft' balls occur when the temperature has not been high enough, so that the mass never got beyond the thinner state to

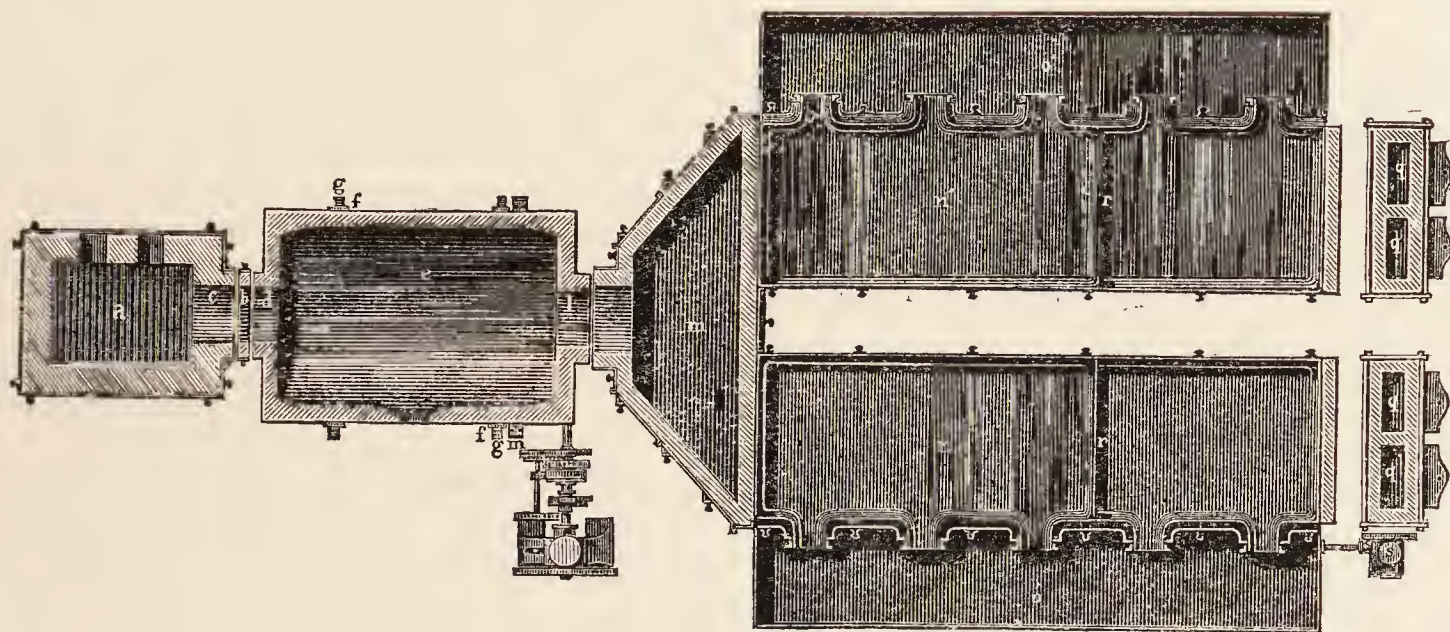


FIG. 4.

the pasty, porous one. Such black ash is very difficult to lixivate, and contains much undecomposed sulphate.

In order to check the furnace men, samples are taken from each man's work, sometimes even from every single ball, and are roughly tested for their percentage of alkali, of sulphate, and of sulphide; but as these cannot be average samples, the judgment of a practised eye on the appearance of the ball in general must always be taken into account as well. The testing-methods are the same as those used for tank liquor (*see* p. 16), col. 2, par. 3).

The following abstract of an analysis on good black-ash ball by Davis (*Chem. News*, 30,

176) shows the complicated nature of the material:—

Dis- solved by water.	Na_2CO_3	NaOH	NaCl	Na_2SO_4	Na_2SO_3	$\text{Na}_2\text{S}_2\text{O}_3$
	31.8	7.2	2.6	0.2	0.1	0.9
Insoluble in water.	Na_2S	$\text{Na}_6\text{Al}_2\text{O}_6$	Na_2SiO_3	NaCN	NaSCN	FeS
	0.2	0.8	0.9	0.04	0.02	0.0

Insoluble in water.	CaS	CaCO_3	Na_2CO_3	CaO	Al_2O_3	SiO_2	MgO
	28.7	8.9	0.9	10.0	1.0	0.9	0.3

	FeS	C	Sand
	0.8	4.5	0.9

Revolving black-ash furnaces.—The work done in a ball-furnace consists in keeping the charge turning over, and this can be done

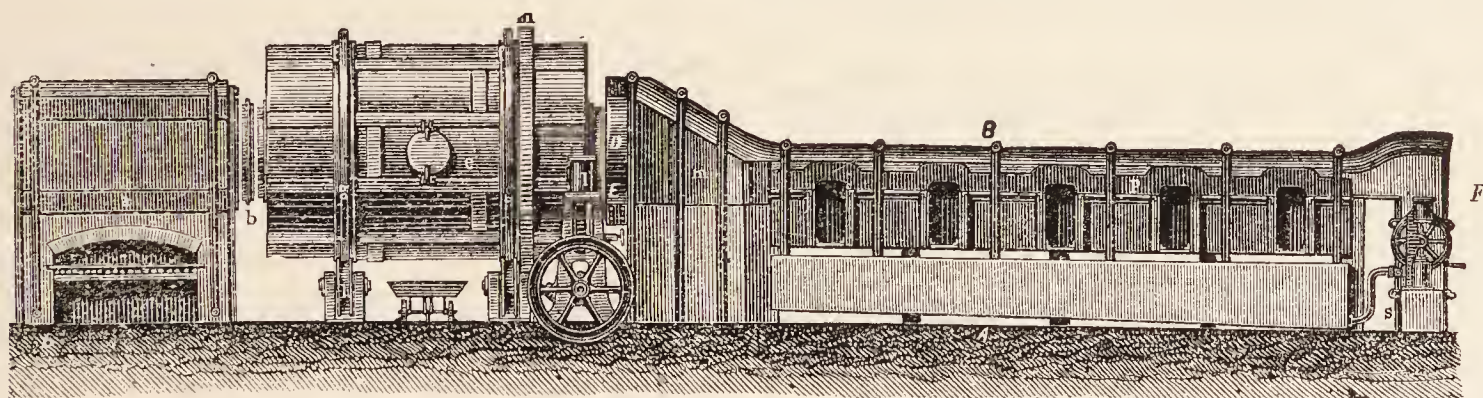


FIG. 5.

most efficiently and at least cost by mechanical means. The making of an efficient mechanical furnace proved, however, a difficult task, even after the right principle, that of a cylindrical furnace revolving as a whole, had been found by Elliott and Russell, in 1853. Apart from the mechanical imperfections of their furnace, it turned out black ash much too hard and in a very bad state for dissolving, because by the continuous rotation all the gas was driven out, and the honeycombed structure of the balls was lost. Stevenson and Williamson, in 1855,

overcame both difficulties, and they must be called the true originators of mechanical black-ash furnaces, usually called 'revolvers.' By experiences upon the Tyne they were made entirely practical about 1863, and were then introduced into Lancashire; they entirely superseded the hand furnaces.

Figs. 4 and 5 show an ordinary revolving black-ash furnace in sectional plan and in elevation: *a* is the fireplace, with two feeding doors and a cylindrical opening, $2\frac{3}{4}$ ft. wide, for the flame to pass through. Between this

and the revolving cylinder there is a cast-iron ring *b*, the 'eye,' lined with fire-brick hung by means of chain and pulleys, which allows some air to enter all round, and the necessary expansion to take place. The cylinder *e* consists of a shell of $\frac{1}{2}$ -in. boiler plates, $15\frac{1}{2}$ ft. long and $10\frac{1}{4}$ ft. wide inside; cast-iron tire seats *ff*, and cast-steel tires *gg*, are shrunk upon the barrel, and work upon the V-rollers *h*. The cylinder is lined inside with fire-bricks, 9 ins. thick in the centre, $1\frac{1}{2}$ ft. at the ends; this facilitates the running out of the charge. Two horizontal 'breakers' of fire-brick blocks project inwards from 9 to 13 ins. from the other lining, and promote the mixing of the charge in revolving. A $1\frac{1}{2}$ -ft. manhole closed by an iron lid allows charging and emptying the furnace. Each furnace is provided with a special engine, possessing double gearing so that it can produce either a slow movement (one revolution in 10 mins.) or a quick movement (five revolutions per minute). The gearing acts upon a great spur-wheel *m*, made in one piece and bolted immovably to the furnace. The exit opening *l* communicates with the large dust chamber *m'*, to which are joined the two boiling-down pans *n* and *n'*, 28 ft. long by 8 ft. wide by $2\frac{3}{4}$ ft. deep (each with their drainers *o* and *o'*), and from these the products of combustion go through the flues *qq* into a chimney. The purpose of the pans is described later under *Evaporation to monohydrate* (see p. 171, col. 1, last par.).

A tramway runs above the furnaces for charging them, and another (smaller) tramway runs underneath them for moving the train of discharging trolleys or bogies into which the finished charge is run from the revolver.

A furnace of this size takes charges of 30 cwts. salt-cake and gets through 15–18 tons of salt-cake in 24 hours, with a consumption of 10–13 cwts. of firing fuel per ton of salt-cake. Much larger revolvers have been erected, a common size being 18 ft. in length by 10 or 12 diameter. Such a revolver will decompose a 3- or 4-ton charge of salt-cake in 2 hours. The largest revolvers made are, one erected by the Widnes Alkali Co., in 1887, 30 ft. long and 12 ft. 6 in. in diameter (described by Watson Smith in the *J. Soc. Chem. Ind.* 1887, 417), which decomposes a charge of 8 tons 12 cwts. salt-cake in $3\frac{1}{2}$ hours; and one at the works of Messrs. Kurtz, St. Helens, which is 30 ft. 6 ins. long and 12 ft. 6 ins. diameter.

There has been much controversy as to the best way to mix and work the charge in a 'revolver.' The various methods suggested had for their object: (1st) The production of a more porous and more easily lixiviated black ash, and (2nd) the destruction of the cyanides formed in the ordinary process which are responsible for carrying iron forward in a soluble form to the end of the process.

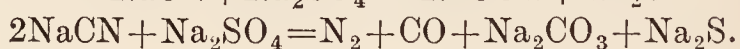
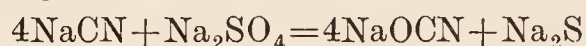
The following methods of working the charge have been practised:—

1. The chalk or limestone and two-thirds of the coal are introduced and the revolver kept slowly turning round till on inspection through the manhole the appearance of a blue flame of CO shows some caustic lime has been formed. This liming process lasts 1– $1\frac{1}{2}$ hours. Then the salt-cake, together with the remainder of the

coal, is added and the rotation slowly continued until the mass is nearly fused, when the quick movement is started. The object of 'liming' is to produce a certain proportion of caustic lime, which in the lixiviating tank will cause the balls to burst, and to be more easily dissolved.

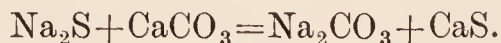
2. Mactear in 1874 patented the following method of work. He charges the salt-cake, coal, and limestone at once, but only uses the theoretical quantity of limestone. When the black ash is formed and the charge is fused he stops the revolver and adds quicklime equal to 10 p.c. on the weight of the salt-cake, and 15 p.c. of cinders with the objects of: having present sufficient quicklime to make the lixiviation easy; to make the mass porous by the presence of the cinders; to cool the mass previous to its pouring out; to economise in materials; and to increase the output of the revolver. The success of this method is a direct proof of the incorrectness of Thenard's and Dumas' theory that alkali waste was calcium oxysulphide. The liquor made from Mactear black ash contained per 100 parts of total alkali 1.0 to 1.06 parts of sodium ferrocyanide. The sodium sulphide is rather high and leads to difficulties in subsequently preparing the ash or soda crystal.

3. Péchiney in 1877, knowing that the very objectionable ferrocyanide in the black-ash liquor was formed from the sodium cyanide in the black ash when the solid was lixiviated, found that the sodium cyanide was only present when the black ash is finishing, that is, when the sodium sulphate is almost all converted into carbonate, and that if to the finished charge of black ash containing sodium cyanide he added sodium sulphate, the cyanide is promptly destroyed by its reducing action on the sulphate, according to one of the reactions



This process was patented December 24, 1877, and January 11, 1878.

Weldon recognised that the sodium sulphide generated in the Péchiney process above required treatment, and he patented, January 11, 1878, the addition of a corresponding amount of powdered limestone along with the sodium sulphate, to react as in Leblanc's original process.



The combined Péchiney-Weldon process reduced the ferrocyanide forming in the black ash liquor to a maximum of 0.29 and a minimum of 0.03 per 100 of total alkali; and since the source of the cyanide in the black ash was the nitrogen content of the coal (1–1.5 p.c.) the excess of coal previously employed was abandoned. The disadvantage of this process was that it increased the amount of sodium sulphate going into the black ash liquor and thence into the soda ash. This process was used in many works.

Several other patents were taken out directly afterwards by Mactear, Gaskell, Brunner, Allhusen, and Pauli, all aiming at the oxidation of the cyanides just before drawing the black ash, but their success was not as great as that of the Péchiney-Weldon process.

4. The following are attempts to destroy the cyanogen compounds in black ash, after that the black ash had been withdrawn from its furnace.

Newall and Sisson, and later Mactear, showed if the still hot black ash cake is broken into small pieces and exposed to the air, that ammonia is evolved and the proportion of cyanide much reduced (J. Soc. Chem. Ind. 1887, 349).

Mathieson and Hawliczek (Eng. Pat. 5456 of 1886) introduced a method of decomposing the cyanide, sulphocyanate, and cyanate in finished black ash, in that after a few hours' cooling it was broken mechanically into 3-in. to 5-in. pieces and charged into large wrought-iron cylinders, heated externally by waste heat from the black-ash revolver to 370°–420° and through which steam was blown, and from which the excess steam and the produced ammonia were led away for recovery of the ammonia (J. Soc. Chem. Ind. 1889, 351).

5. None of these processes appears to be necessary, and the latest practice was to drop the whole charge into the revolver at once and work it through without stoppage or addition. The following may be taken as the normal mixing for a black-ash revolver under those conditions:—

Salt-cake	55 cwts.
Limestone	56 „
Slack	22 „

Black-ash Tests and Properties.

The following tests are abstracted from published records and give some idea of the composition of black ash made in revolvers. The analyses are very difficult, because the black ash absorbs moisture, carbon dioxide, and oxygen from the air, because there are so many substances present, and a number of these suffer changes during the analysis, and because some of the analytical methods for these complex mixtures are not easy or good:—

Mixing and analysis	Muspratt, revolver, July 1874	Muspratt, Mactear's revolver process, April 1886
Salt-cake	100	100
Limestone	106	78
Coal 10 p.c. ash.	55	47½
Finishing lime	—	7½
Na ₂ CO ₃	41·6	46·2
NaCl	1·2	0·7
Na ₂ SO ₄	1·2	0·4
Na ₂ SO ₃	0·14	—
Na ₂ S ₂ O ₃	—	0·6
SiO ₂	2·4	2·7
Al ₂ O ₃	1·1	0·8
Fe ₂ O ₃	0·9	1·0
CaCO ₃	11·6	9·7
CaO	5·7	1·7
CaS	29·8	33·6
MgO	—	0·4
Coke	4·4	3·5

The following is a partial analysis of black ash made by the Pechiney-Weldon process:—

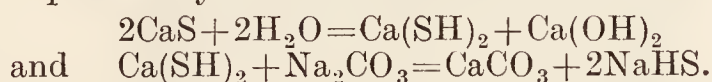
Salt-cake	100
Limestone	77·8
Coal	36·1
Na ₂ CO ₃	41·46—44·46
Na ₂ S	0·31—0·48
Na ₂ SO ₄	0·18—0·90
Total Na ₂ SO ₄ after oxidation	0·88—1·90
Alkali in soda waste	0·19—0·23

Black ash contains a small amount of sodium cyanide, which can be detected by extracting the powder with alcohol which dissolves the cyanide. When the black ash is extracted by water in any ordinary way the cyanide is quickly converted into ferrocyanide.

Black ash keeps unchanged in the absence of moisture and carbon dioxide, but in the presence of these it soon undergoes a change (studied by Kolb, Ann. Chim. Phys. [iv.] 7, 118; 8, 135; 10, 106). The lime attracts both H₂O and CO₂; on being hydrated it swells up and cracks the balls, which gradually fall to powder. On lixiviating, they now yield less NaOH, but, on the other hand, much more Na₂S and products of its oxidation, since the action of the atmosphere on CaS produces calcium hydrosulphide, polysulphide, thiosulphate, and other soluble calcium compounds which, on lixiviation, at once react on sodium carbonate. Black ash on keeping always deteriorates even to the extent of becoming useless, and therefore ought not to be kept too long before working it up, and ought to be so stored that it is protected from the access of changing air.

Lixiviation of Black Ash.

The action of water on black ash has been studied by Kolb (Ann. Chim. Phys. 1866, 35). From his experiments he draws the following conclusions. The quantity of NaOH formed in the lixiviation vats, by the action of lime on sodium carbonate, is not materially influenced by the quantity of water, but increases both with the time of digestion and the rise of temperature. Almost exactly the same conditions govern the formation of sodium sulphide, which may be expressed by the two reactions:—



The temperature of the strong washing liquors run on to the new black ash may be 60°, because such liquors act less readily on CaS than weaker solutions or water, but the temperature of the fresh water run on to the nearly exhausted calcium sulphide should not be much above 32°.

The black ash should be broken into lumps of about 6 inches diameter, so that there are passages between the lumps to allow the strong solution formed to readily fall away. During the lixiviation the solids should not be disturbed, otherwise the liquor becomes muddy. The lumps of black ash must be entirely submerged under the liquor, otherwise a rapid oxidation of CaS occurs to polysulphide, thiosulphate, and sulphate; all these soluble calcium salts render useless corresponding amounts of sodium carbonate.

Various forms of apparatus have been used, but they were all displaced by the form originally

invented by Professor Buff, of Giessen, and first brought into practice by Dunlop, at St. Rollox, in 1843. It made its way into Lancashire about 1860, and in England it seems to have been dominant about 1864, and on the Continent 10 years later. In this country it is generally known as Shank's process. Its principle is to allow the black ash to remain in the same place, and to cause the liquor to move forward in a methodical manner, so that it is brought up to concentration, and the black ash is completely exhausted at the same time, without ever being

exposed to the air; by this course the liquors are much stronger and purer, and the process is much less expensive than with the plans formerly practised.

The way of carrying out the process is shown in Fig. 6. A number of 'tanks' or 'vats'—at least three, more commonly four, but sometimes five, six, or even more—is combined to form a set. The tanks must be all on the same level, and this should be so far removed from the ground, by means of pillars, that no leaks can occur without being observed. They

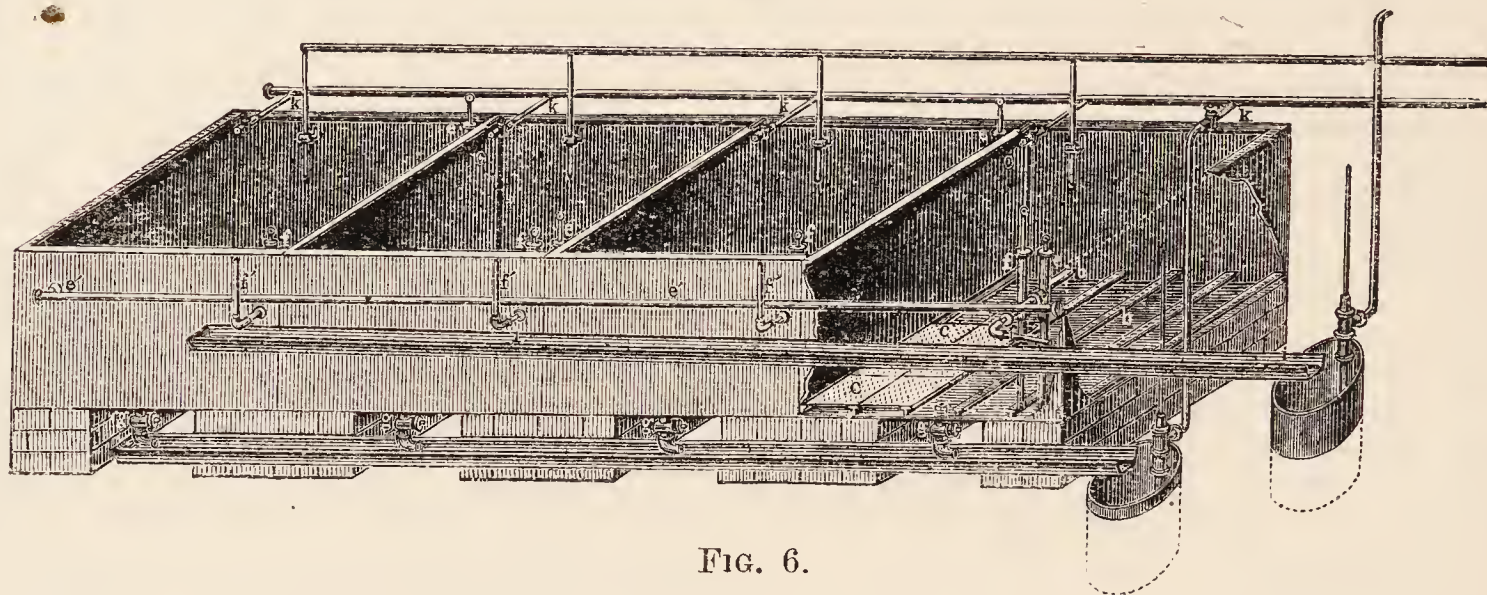


FIG. 6.

are made of wrought iron. Near the bottom there is a row of T-irons *bb*, for supporting the perforated plates *cc*, forming a false bottom. Whilst the true bottom is often made to slope to one side, where the outlet cock is placed, the false bottom must be quite horizontal (see Fig. 7).

The liquor traverses the tanks in the order 1.2.3.4 from left to right in Fig. 18; then 2.3.4; 2.3.4.1; 3.4.1; 3.4.1.2, and so on, by means of the following arrangements of pipes and cocks.

Each of the tanks contains two overflow

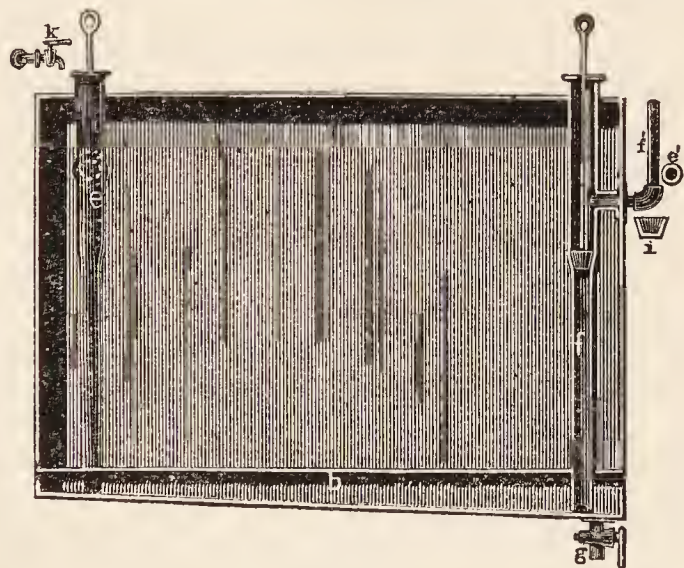


FIG. 7.

pipes, one, marked *e*, for weak liquor, and another, marked *f*, for strong liquor. The construction of these overflow pipes is best seen on the section, Fig. 7. They are cast-iron pipes, a little wider in the upper part, with a conical plug fitting into a seat bored out at the enlargement. Above the plug-seat the pipe has a side-branch, bolted to one side of the tank, where there is a corresponding hole.

In the case of the *e* pipes this hole is always in the side adjacent to the next tank, and also so placed that the direct course from pipe to

pipe forms a series of diagonals across the tanks; but in the case of tank 4 the hole is in the front of the tank and the liquor then passes by the long pipe *e'e'* into tank 1. The pipes pass through the false bottom, so that only the liquor below the false bottom can enter into them. If a plug marked *e* is taken out, the liquor contained in the tank will rise from its bottom in the pipe *e* and will overflow into the next tank near its top. Where, however, it is intended not to run the liquor upon the next tank, because it is concentrated enough to be run off, the pipe *e* will be kept closed and the plug taken out of pipe *f*.

All the pipes *ff* are arranged on the front side of the set; they are, on the outside, provided with swivel-pipes *f'*, which, when turned up, prevent the liquor from running out. By turning the branches *f'* downwards at the same time as the plugs are taken out, the strong liquor runs into the shoot *i*, and from this into the well, from which it is lifted by the injector shown into the settlers which are not shown.

At some works there are cocks instead of the swivel-pipes *f'*; at others the strong liquor pipes *ff* are omitted, and the strong liquor is run off by means of the bottom-cocks *gg*, which must be provided in any case; but neither of these plans can be recommended.

The bottom cocks *gg* serve for running away the weak liquor previously to casting out the solid waste. This liquor passes on to a separate well, from which it may be lifted by the injector shown into the water-conduit *k*, from which the tanks are supplied by a separate branch each. The uppermost set of pipes serves for supplying either steam or hot water, as the case may be.

The starting and working of the lixiviation vats is carried out as follows: Each of the four vats shown in Fig. 18 is charged with lumps of

black ash, broken by a sledge hammer to pieces such that a man can readily handle them, until the lumps reach to about 1 foot from the top. The water supply is then opened to tank No. 1, and the *e* valves in tanks 1, 2 and 3 are opened, and the *f* valve and swivel pipe in tank No. 4. As the tanks fill with water the temperatures are regulated by the steam supply pipes, so that the temperatures vary gradually from about 35° in No. 1 tank to about 60° in No. 4 tank, for reasons already given. The overflow from tank No. 4 may register 56°Tw., but as the process goes on this strength gradually falls. A watch has now to be kept on the liquor leaving tank No. 1, as the strength of this constantly falls until it registers 0° on the Twaddell hydrometer. No. 1 tank is now finished washing, the water supply is stopped, the cock *e* is closed, the cock *g* is opened, and all the liquor is run off and then blown up into the weak liquor store tank. When the insoluble tank waste has drained, it is thrown out, and the tank is recharged with fresh black ash. Tank No. 2 must now be made the first in the series, and tank 1 the last in the series; the weak liquor store tank is started to run into No. 2 tank, thence through tank 3 into tank 4, in which cock *f* has to be now closed and cock *e* opened so that the fairly strong liquor flows into tank No. 1, from which it flows by opening its cock *f* and lowering *f'*. This arrangement continues until the weak liquor tank is empty, when fresh water is started to run into tank No. 2, and continues until the liquor leaving No. 2 tank falls in strength till it registers 0° on the Twaddell hydrometer. No. 2 tank is now ready for draining and emptying, and so the process goes on, emptying in subsequent succession tank 3, tank 4, tank 1, tank 2, &c. The average strength of the liquor accumulating in the strong liquor settling tank is about 46°Tw.

The vat liquor is always too muddy for immediate further treatment, and must be *settled* first.

From the vats the liquor was pumped into settlers, where it was kept sufficiently warm to avoid crystallisation of the $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$. This will cause the vat waste mechanically carried away to subside; at the same time the action of the air will cause some of the ferrosodium sulphide to be decomposed, and the FeS to be deposited along with alumina and silica, partly or entirely in the state of chemical combination.

The insoluble residue that is emptied out from the tanks, 'tank waste,' if properly extracted contains very few pieces larger than a pea, and is not muddy; in colour it is bluish or blackish-grey. It was dumped into great mounds or into great tanks made with moveable wooden shutters, and there set into miniature mountains, the drainage from which poisoned the water courses, and the sulphuretted hydrogen gas evolved from the mounds made the air objectionable in all the vicinity, tarnishing all brass, silver and copper, and making all white lead paints of the colour of metallic lead; and many of the proposals for new processes of making sodium carbonate have been influenced by the great inconveniences arising from Leblanc's tank waste. Owing to oxidation the mounds may fire and evolve sulphur dioxide. In

Widnes, where 1000 tons of waste were deposited per day, there are more than 500 acres covered. On the Tyne the waste is carried out to sea in hopper barges and dumped there.

Tank waste contains up to 4 p.c. Na_2CO_3 reckoned upon the dry waste. A great variety of suggestions have been made for utilising tank waste, and many methods have been tried for recovering the sulphur contained in its calcium sulphide. This quest was begun by Gossage in 1837, but only in 1888 was economical success obtained by Chance and Claus, who decomposed it by carbon dioxide to obtain sulphuretted hydrogen and calcium carbonate, the first of which was burnt with a limited air supply to obtain sulphur and water, and the latter was used for making Portland cement (J. Soc. Chem Ind. 1888, 162; Lunge, vol. ii. part 2, 889 to end; this Dictionary, 1st edition, under SULPHUR and also SODIUM). Chance also drew attention in his original paper to the value of the water filtered from the Chance waste for use on the black-ash vats, to which it would return quite an appreciable part of the total soda loss on the Leblanc process (cf. Eng. Pat. by Carey and United Alkali Co., Ltd., 7404, 1911). The description of the details of the process, though proper in the description of alkali works, are not proper to this article on SODIUM CARBONATE, and further details must be found from the above references.

Testing methods for black ash, vat liquor, and tank waste.—In order to test *black ash*, a sample consisting of several pieces of the ball (which unfortunately can never be a real average sample) is finely powdered, and 50 grms. of it are digested with tepid water, free from oxygen and carbonic acid; the solution is made up to 500 c.c., and is now tested just like the tank liquor obtained on the large scale. 1st, for *total available alkali*, by means of standard hydrochloric acid and methyl orange; 2nd, for *caustic*, by addition of barium chloride filtering and titrating the filtrate with hydrochloric acid, or by titrating with oxalic acid without filtration; 3rd, for *sulphide*, by means of iodine; 4th, for *sulphate*, by means of barium chloride, either gravimetrically or volumetrically; 5th, for *total sulphur*, by oxidising with bleaching powder and estimating the sulphate formed; 6th, for *chloride*, by standard solution of silver nitrate, after having exactly neutralised the alkali by nitric acid and boiled away the H_2S ; 7th, for *ferrocyanide*, by means of Hurter's copper sulphate solution. *Vat waste* is mostly only tested for *available soda* by treating with CO_2 , boiling, filtering, and titrating the clear portion; sometimes also for *total soda*, including the *insoluble* portion, which is a somewhat lengthy process. (Details of all these methods are given in Lunge's Technical Chemists' Handbook.)

Jurisch (Chem. Ind. 1880, 441) recorded analyses of the impurities in vat liquors from which the following are abbreviated (see table, p. 170); they are calculated upon such a volume of vat liquor as contains 100 total parts of available alkali (Na_2O).

Purification of the Liquor.

Whatever way the black-ash liquor is subsequently treated, and whether the products

	Muspratt hand furnaces, 16 days' average	Muspratt revolvers, 30 days' average	Runcorn Soap and Alkali Works		More recent practice, average
			Péchiney revolver, average	Péchiney- Weldon, average	
NaOH	43.4	27.5	17.1	24.6	32.3
NaCl	7.3	5.9	—	—	3.0
Na ₂ SO ₄	6.0	1.7	4.1	3.6	2.3
Na ₂ SO ₃	0.4	0.2	—	—	—
Na ₂ S ₂ O ₃	1.1	0.7	1.5	1.0	—
Na ₂ S	1.4	2.1	1.4	2.2	1.0
Na ₄ FeCy ₆	0.1	0.4	0.2	0.2	—
SiO ₂ , Al ₂ O ₃ , Fe ₂ O ₃ .	2.7	2.4	—	—	—
Mixing proportions :					
Salt-cake 96 p.c. . .	100	100	87.8	100	—
Limestone	102.1	76	64.4	74.4	—
Coal	52.1	38	34.8	41.9	—
Mactear lime	—	8.3	—	—	—
Péchiney salt-cake . .	—	—	12.2	11.6	—
„ limestone dust . .	—	—	7.3	7.0	—
Sifted cinders	—	10	—	—	—

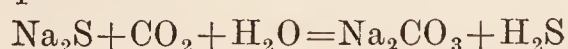
desired are soda ash, or monohydrate, or decahydrate, the impurities in the liquor, though at first overlooked and ignored, have received much attention of more recent years, so as to obtain always purer grades of product, and these impurities more often than not then determine the whole course of the proceedings. These purifying proceedings, in so far as they were effected in the mixing of the black ash either before it was lixiviated, or in the lixiviation have already been described. The purifications of the liquors are briefly as follows:—

(1) Removal of all forms of sulphides, including sodium ferrous sulphide by precipitation, as a metallic sulphide. In 1804 Clayfield used zinc hydroxide and zinc carbonate, and D'Arcet did the same in 1828; in 1878 Parnell dissolved metallic zinc in the liquor by reason of its caustic soda content; in 1883 Glover again used zinc carbonate; and in 1904 Stuckle again used metallic zinc.

Iron compounds were also used, Kolb using ferrous sulphate; Deacon used ferric hydrate; Habich used native ferrous carbonate; Chance in 1885 precipitated ferric chloride with an excess of lime and used that mixture.

Lead compounds were also used; lead sulphate, a by-product in making aluminium acetate, was used at Dieuze; lead oxide or its solution in caustic soda by Owen in 1885.

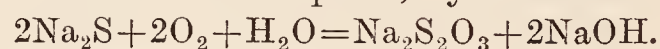
(2) Removal of the sulphides by treatment with carbon dioxide. In 1841 Gossage (Eng. Pat. 8973 of 1841) ran the black-ash liquor down a pebble-filled tower into which carbon dioxide was passed, which was supposed to decompose the sulphide thus



but as he used waste fire gases containing not inconsiderable amounts of oxygen, the reaction was not as above, and will be considered under (4). In 1847 Beringer pointed out that only lime-kiln gas is practically available, and that it is impossible to remove all the sulphide while keeping the sodium as Na₂CO₃ (see p. 175, method 10, under *Preparation of sodium car-*

bonate from Na₂S and CO₂, 1819; and under *Sodium bicarbonate*, p. 181, col. 2, par. 2).

(3) Removal of all forms of sulphide, including sodium ferrous sulphide, by oxidation



In 1841 Gossage (see above) passed waste gases containing some oxygen over descending streams of black-ash liquor, but in 1853 (in Eng. Pat. 18th May, 1853) he described the treatment with air. The liquor should be 42°–50°Tw. and hot, and by pumping the liquor through the tower several times the liquor at last lost all its colour, and tested with lead paper ceased to give a reaction for sulphides; the accompanying sodium ferrous sulphide is similarly converted into the sulphate and into insoluble ferrous sulphide or ultimately ferric oxide. Owing to the difficulty arising from the precipitate, Gossage's towers were replaced by large open tanks for the liquor, and air was forced through a multiplicity of holes in a deeply immersed perforated plate (Hargreaves), and the operation was complete in a few hours.

In 1879 Pauli patented the addition of a very small quantity of Weldon mud (Calcium Manganite CaO·2MnO₂. See under CHLORINE, Weldon's Manganese dioxide recovery, vol. ii. pp. 186 to 191), which, acting as a catalyst, the oxidation proceeds with greater rapidity and completeness, but it has the disadvantage that a trace of manganese may get into the solution and then the soda ash subsequently prepared has a bluish colour from sodium manganate.

(4) Removal of caustic soda by treatment with carbon dioxide



This purification takes place when the black-ash liquor is treated as in (2), and it makes no fundamental difference whether the gas employed contains oxygen or not; the treatment is controlled by testing the liquor with turmeric paper and using as a standard colour a turmeric paper dipped in a pure strong solution of sodium carbonate; if the treatment is continued past this test then sodium bicarbonate begins to form.

(5) Removal of sodium aluminate, sodium silicate, by treatment with carbon dioxide. When the black-ash liquor is treated as in (2) the sodium aluminate is readily decomposed by carbon dioxide

$2\text{NaAlO}_2 + \text{CO}_2 + 3\text{H}_2\text{O} = \text{Na}_2\text{CO}_3 + \text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$
or rather the equation given, p. 178, Method 15, which describes the manufacture of sodium carbonate from sodium aluminate solution and carbon dioxide. Sodium silicate is not nearly so readily decomposed, but if the solution contain both sodium aluminate and silicate, then the precipitating alumina and the passing carbon dioxide together entirely decompose the silicate provided there is a sufficiency of the aluminate, the precipitate appears to consist of aluminium silicates. The black-ash liquor also contains small quantities of lime salts, and when the liquor is carbonated these are precipitated in the form $\text{Na}_2\text{CO}_3 \cdot \text{CaCO}_3 \cdot 5\text{H}_2\text{O}$, which occurs native as Gay-Lussite, and is probably the form in which the insoluble soda is held in the insoluble black-ash waste. All these precipitations were made known by Gossage's patent of 1841, mentioned under (2); the difficulty they caused by blocking up Gossage's pebble or coke-filled towers was so considerable that they were replaced by Hargreaves' bubbling tanks described under (3).

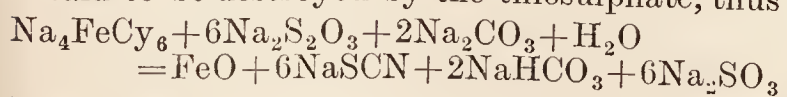
In 1881 Carey, Gaskell and Hurter patented the addition to the liquor under carbonation, of bauxite, native $(\text{AlFe})_2\text{O}(\text{OH})_4$, with the object of accelerating and completing the decomposition of the sodium silicate, and in doing this they have advised that about one-twentieth of the total soda should be converted into bicarbonate.

(6) Removal of all forms of sulphides, including sodium ferrous sulphide, caustic soda, sodium aluminate, and silicate, &c., by adding a small amount of calcium manganite and the required quantity of bauxite, and blowing through waste black-ash furnace gases, was patented in 1880 (Eng. Pat. 608) by Carey, Gaskell and Hurter. This is a summation of the previous paragraphs (2), (3), (4) and (5).

(7) Removal of sodium ferrocyanide. This objectionable impurity is formed from the sodium cyanide in the black ash by secondary reactions occurring in the lixiviation of the black ash, and the means taken to reduce the amount of cyanide have been already described under black-ash process, especially under the revolver furnaces which produce most cyanide.

In 1866 Williamson proposed to destroy the ferrocyanide by heating the black-ash liquor under pressure in a boiler to 155° ; the process was incomplete and could not be carried out because of the incrustations forming in the boiler.

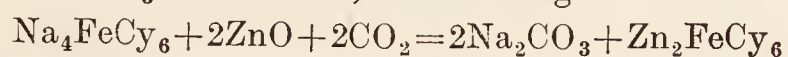
In 1879 Carey, Gaskell and Hurter (Patents 2939, 1879; 1161, 1881; 5310, 1882), after applying their purifying process referred to in (6), passed the clear liquid through 1200 feet of iron pipe, two-inch bore, heated in a furnace and provided with an exit valve loaded to give about 260 lbs. per sq. inch. The ferrocyanide is said to be destroyed by the thiosulphate, thus



The treated liquor is settled, run off, and oxidised

with air. The process is complicated and has only been used by the inventors for preparing 'crystal carbonate.'

In 1887 Newall and Sisson (J. Soc. Chem. Ind. 1887, 349) record that when black-ash liquor has been oxidised and carbonated by treatment with furnace gases, and clarified (as in paragraphs (2), (3), (4), (5), (6) above) and evaporated and cooled to obtain $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ that the mother liquor contains the accumulated ferrocyanide to the extent of up to 5 p.c. of the total alkali present, and when evaporated to dryness and calcined give a dark red or brown ash that had necessarily to be purified. They found that the mother liquor could be freed from ferrocyanide by adding a zinc salt or zinc oxide and blowing in some carbon dioxide till some NaHCO_3 was formed, and filtering



The filtrate on evaporation and calcination yielded a white ash. The zinc ferrocyanide was decomposed by a calcium hydrosulphide solution to obtain a solution of calcium ferrocyanide, and thence Prussian blue or potassium ferrocyanide; the zinc sulphide was converted into zinc oxide.

(8) Removal of thiocyanates, sulphates, thiosulphates, and chlorides cannot be effected on the liquor itself, but during the following evaporation either for decahydrate, or much more generally for monohydrate, the impurities accumulate in the mother liquor, but sulphate in moderate proportion crystallises with the decahydrate.

Evaporation of Vat Liquor.

The original method of evaporation was very remarkable, it was to run the unpurified vat liquor into pans set over a waste heat, whereby it was concentrated to about 60°Tw. and was then run into a reverberatory furnace lined with firebrick, the firebrick floor of which was covered with a previously obtained layer of soda ash, and the whole furnace hot before the liquor was admitted. The liquor, when admitted, soon evaporated to a paste, which was constantly raked to present fresh surfaces to oxidise the sulphides and ferrocyanides, &c. The mass becoming harder was carefully worked and roasted till it changed from reddish to white. The destruction of the sulphides was tested on a sample by adding a lead solution. The greatest care had to be exercised not to fuse or cake the mass by reason of the ready fusibility of the accompanying caustic soda. The finished mass was raked into iron barrows to cool, and was broken and sifted. This method was largely used; in France the furnaces were known as Marseilles Furnaces, and in England as Dandy Furnaces. The product was known as caustic soda ash, and its percentage composition varied from Na_2CO_3 61-77, NaOH 10-24, and the remainder all the impurities of the vat liquor as changed by the roasting and fire gases. This form of soda ash was not suitable for many industries, notably for wool scouring.

A great improvement was made by separating the initial evaporation and the final ignition into two distinct processes, separated by the formation of crystals of $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$, the advantages being the utilisation of the waste

heat from the black-ash furnaces for the initial evaporation, and the possibility of obtaining much purer qualities of soda ash. Figs. 1, 2 and 3 (see p. 164) show on the right-hand side the large evaporating top-heated pan attached to a hand black-ash furnace, and Figs. 4 and 5 (see p. 165) show also on the right-hand side the large evaporating pans attached to a mechanical black-ash furnace. In the former apparatus the settled vat liquor was run into the pan shown with two working doors; in the latter apparatus it was run into the two pans *nn'*, after that the three working door plates had been put into place with a jointing of lime putty or of clay and been bolted tightly, and until the pan was nearly full of liquor.

The fire gases from either kind of furnace passed over the surface of the liquor in close proximity to the liquor because of the low confining arches shown in Figs. 2, 3 and 5. As the liquor diminished, its volume was replenished by more vat liquor from the settlers. It was at first desired to convert the caustic soda impurity in the vat liquor into sodium carbonate, and for this purpose soft wood sawdust was added to the liquor in the evaporating pan.

Crystals of $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ formed first on the surface of the liquor nearest to the fires, and these crusts greatly hindering the evaporation were pushed down by the pan men by long-handled rakes worked through the small opening above the door plate seen in Fig. 3 on the right hand, and at the same time they raked the deposited crystals to the colder end of the pan. This work continues until the contents of the pan are converted into a mixture of the consistency of mortar.

The door bolts were then slacked back; some mother-liquor ran into the drainer in front of and below the doors shown in Figs. 1, 3, 4, *o* and *o'*, and in 5, upon the perforated false bottom of which was frequently spread sawdust to aid the filtration and to aid in the following roasting. The doors were removed completely and the whole pasty mass drawn out, the doors replaced, and the process begun again. In Fig. 16 the two pans shown in parallel between the fire and the chimney are drawn alternately after the closing of pan dampers, so that the firing of the revolver is not interrupted. The pan salts were drained until the drainer was required for the next batch, and then removed to other drainers, washing tanks, or centrifugals, and further drained or washed according to the degree of purity required. The colour should be greyish-white, but the workman's name was 'black salt'; some of the colour was due to the fire ashes falling from the fire gases into the evaporating pan.

A well-drained monohydrate contained 91.3 p.c. $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$, 0.9 p.c. insoluble, and the remainder mother-liquor with its due proportion of accumulating impurities.

The mother-liquor from its colour was known as 'red liquor,' this was due to the sulphides and to organic matter from the added sawdust; the liquor contained about 3.5 p.c. of $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$, and about 12.6 p.c. of NaOH ; its sp.gr. was just over 1.3.

The red liquor was utilised in different ways, according to the number and qualities

of the grades of soda ash produced at any works.

Where only one grade was made, the red liquor was returned to the pan by the pump shown on the right hand of Figs. 1 and 3, and then mixed with the oncoming lots of black-ash liquor, thus losing the advantage of having separated some of the impurities.

Where two grades of soda ash were made the red liquor was pumped by the pump *F*, Fig. 5, also seen in Fig. 4, into one or other of the small pans shown on the right hand of the partitions *rr* shown in Fig. 4, and there either (1) being admixed with sawdust it was evaporated as before, drained, ignited to obtain a soda ash of low strength because it contained the accumulated sulphates, chlorides and other impurities, or (2) it was evaporated alone to obtain an impure and a very caustic ash.

Where the black-ash liquor had been carbonated by contact with flue gases, as described under purification of black-ash (Gossage, 1841, see p. 173, (2)), the red liquor is practically free from caustic soda, and the evaporation was then continued until the $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ deposited, reached its lowest limit of purity for conversion, and after that the salts deposited, containing very much sodium sulphate, were only fit to be mixed with the next charge for the black-ash furnace.

The recovery of the caustic soda from the red liquors is described under the heading of *Sodium hydroxide* (see p. 241, col. 2, top).

Another form of pan was not provided with the luted and removable doors, but with projecting pockets whose bottoms slope upwards. The deposited salt is drawn by the long-handled rake to this slope, and is then removed by a large fishing shovel with perforated bottom. The first salts so obtained are specially pure and give refined ash, then follows salts for ordinary and for weak ash, and lastly a red liquor as before.

Another form of pan was the boat pan (see p. 217, Fig. 44), with bottom heat; the drawings of these are similar to those previously described. The advantage is mainly that furnace ashes cannot find their way into the liquor, but the disadvantage is that the location of the boiling being changed from the surface of the liquor to the surface of the pan, the pan scales in a troublesome degree and its repairs are costly.

The manual labour of the preceding pans is avoided by Thelen's mechanical pan (Chem. Ind. 1878, 9), a half cylindrical open pan fired from below; the cylindrical axis is a revolving shaft with many somewhat short arms to which are hinged scrapers, which by their weight touch and scrape the pan, and they are so shaped as to move the salt a little towards the back end of the pan, and as they rise to the edge of the pan and leave it are prevented from spilling liquor or salt by a specially extended edge of the pan which drains them back into the pan. Many of these pans have fully answered their purpose in many parts of the world.

Calcining the monohydrate (black-salt) to make anhydrous sodium carbonate (soda ash).

Where evaporation and calcination are conducted in one and the same furnace, this opera-

tion has already been described (p. 171). In all other cases where the evaporation is conducted in a separate furnace, the calcination was carried out in one of several ways according to the purity of the monohydrate, and the purity required in the soda ash; but the monohydrate was always drained for the purpose of preventing the introduction of undue amounts of liquid into the brick-finishing furnace, as they caused undue deterioration of the furnace.

(1) Conversion of monohydrate containing caustic soda into soda ash also containing caustic soda. The reverberatory furnace employed was direct fired and divided into the hotter end and the colder end by a slight rise in the bed, each bed had its own working door. The moist mixture was charged into the cool end, and the bulk of the drying was done at that end, filling the furnace with a steam mist. The partly dry batch was then moved to the hotter end of the furnace and a new damp batch charged into the cooler end. The work on the hotter batch then required a higher temperature, a little above the melting-point of lead, and frequent turning to prevent the

mass from caking, and lastly, the heat was increased a little more and the mass constantly raked to oxidise sulphides, and destroy ferrocyanides. The ash was somewhat fritted.

(2) Conversion of monohydrate containing caustic soda into soda ash free from caustic soda. The monohydrate was in most cases obtained from an evaporation into which sawdust had been charged along with the liquor, or had been added to assist the draining, and if there were not sufficient more sawdust was added to the drained monohydrate, to the extent of about its own bulk, or an equivalent of small coal was added, and the combined operation of dehydrating, carbonating, and oxidising sulphides to sulphates was known as carbonating. The reverberatory furnace employed was the same as described in (1) above, and was used in much the same way, but after removal of the steam the material requires prolonged turning to bring the decomposing and burning carbonaceous matter into contact with every part of the ash. As the carbonation proceeds the liability of the material to flux becomes less; next the stirring was continued

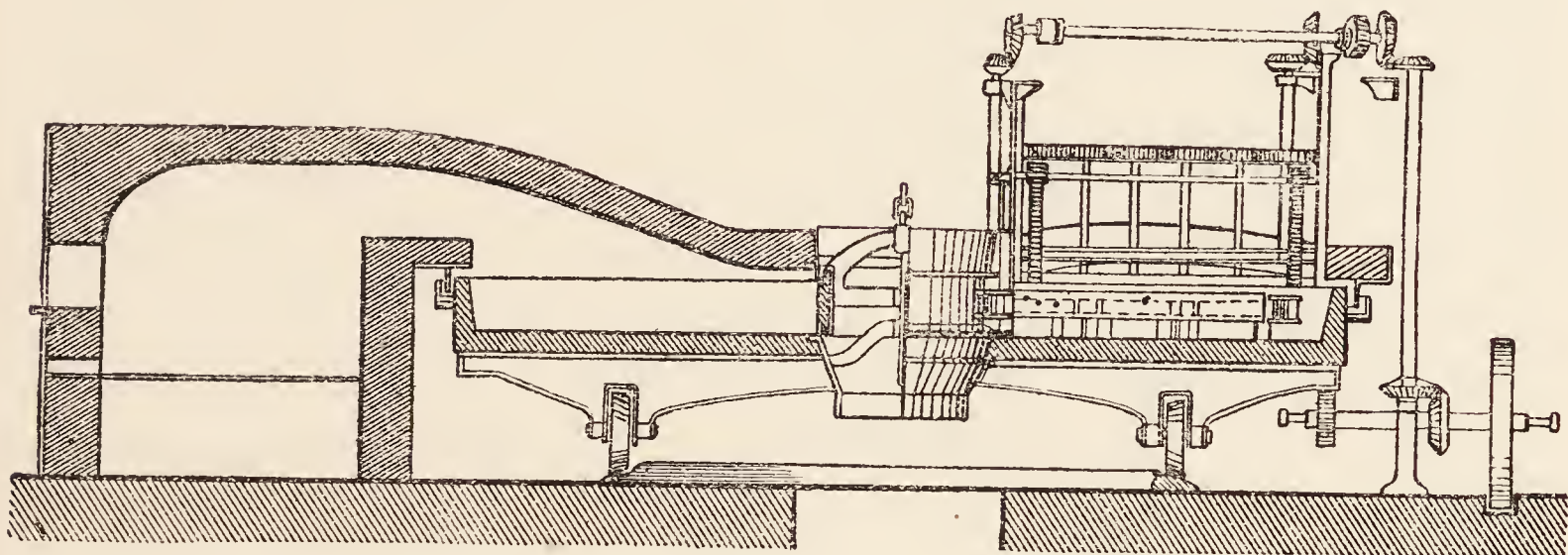


FIG. 8.

to burn off all excess of carbon, and this operation is known as 'cleaning'; lastly, the heat was increased and the mass constantly raked to oxidise sulphides and destroy ferrocyanides as in (1), but the ash produced being free from fluxing is much finer grained than the caustic soda ash. The whole operation took twice as long as the operation under (1).

Mechanical carbonating furnaces were attempted in 1863, but were first made practical by Schofield (Eng. Pat. 511 of 1875), and Mactear in 1876, and this last furnace was largely adopted. Fig. 8 shows the horizontal circular revolving hearth, 20 ft. diameter, made of boiler plate and lined with firebrick, supported on wheels and running on a circular track, and driven by the gearing in the right-hand bottom corner. The furnace on the left has an extension all over the pan except for a narrow rectangular patch containing the stirring arms (on the right hand), a discharging valve (in the centre), two flue gas exit pipes behind and before the stirring shafts (but these flues are not shown), and the charging hopper (not shown), and this extension is made reasonably gas tight by a small hanging curtain that dips into a circular lute surrounding the pan containing sand or soda ash. When the carbonating and roasting are finished the central

discharging valve is sufficiently lifted by a chain (seen in its centre) and a set of scrapers carried on an endless chain (indicated by a pair of dotted lines) and, actuated by the extreme left vertical shaft, is lowered to the revolving hearth and thus empties the pan through the central discharging hole. The ash produced may contain 2 p.c. NaOH or $\frac{1}{4}$ p.c. as desired, is very dense and requires a reduced number of packages, and is whiter, and gives a better settling solution (when it is being used for making soda crystals) than does hand-made ash. A well-drained monohydrate would give a soda ash containing—

					$\text{Fe}_2\text{O}_3 +$	
Na_2CO_3	NaOH	NaCl	Na_2SO_4	Na_2SiO_3	Al_2O_3	MgO
95.4	0.1	0.5	1.1	2.2	0.5	0.2

(3) Conversion of the comparatively pure first drawings of monohydrate from an evaporator, after well draining, into soda ash of greater purity than from (2). Such monohydrate obtained by fishing, from either top-heated, bottom-heated, or mechanical pans, is nearly free from caustic and from sulphides, and if obtained from bottom-heated pans is free from soot and coal ashes, and is therefore not black at all and is very easy to roast, and the reverberatory furnaces are accordingly made larger than

for (1) and (2), little or no sawdust was added and the labour of stirring was reduced, and there was little risk of the batch fluxing. Revolver black ash yielded a purer soda ash than hand-made black ash, and the test of the soda ash then rose to 98 p.c. Na_2CO_3 . To attain the maximum purity only the monohydrate from bottom-heated pans could be employed, and the roasting furnace was fired with gas instead of with coal.

(4) Conversion of comparatively pure monohydrate described in (3) into lightly-fired soda ash. As $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ decomposes below 150° into steam and anhydrous Na_2CO_3 , there is no necessity to heat above that temperature, provided the impurities are small enough in amount to be neglected. This process has the advantage that the waste heat from the under-heated boiling pans is sufficiently hot to dehydrate the monohydrate, so that the waste heat of the black-ash furnace first evaporates the black-ash liquor and then dehydrates the monohydrate. This method was used at Griesheim.

A mechanical furnace for this dehydrating has been devised by Hasenclever of the Rhenania works at Stolberg, somewhat upon the lines of the Thelen pan described for evaporating to monohydrate (p. 172, col. 2, par. 7), and was very economical in labour (Chem. Ind. 1880, 240).

(5) Conversion of very impure monohydrate fished from the evaporating of red liquor in separate pans (when the ultimate mother-liquor is used by preparing caustic soda) into a caustic soda ash. This monohydrate contains so much caustic that it may be gently dried, but cannot be roasted, because it begins to fuse so readily.

Another way of dealing with this special monohydrate was after a batch of ordinary monohydrate was just finished calcining, a moderate quantity of the special monohydrate was thrown on to it and quickly mixed up, and in a few minutes the whole mixing drawn out. The product was a caustic soda ash with about 70 p.c. Na_2CO_3 and 9 p.c. NaOH and other impurities.

Commercial Leblanc soda ash.—As soda ash made by the Leblanc process has peculiarities they are here mentioned: The colour was not white but might be tinted red or yellow from iron oxides, grey from residual free carbon, blue from ultramarine or manganate, and red or black specks from iron oxide or carbon; the caustic soda percentage was generally under 2, sometimes under 1; the insoluble was 1 to $1\frac{1}{2}$ p.c.; sulphides and sulphites were under 0.1 p.c.

To make the ash more suitable for use it was while still warm ground (mostly in horizontal stone mills) and then packed at once in casks, which while filling were mechanically shaken or rammed to reduce the cost of the carriage.

As the soda ash was required of certain specified test, an ash that tested somewhat higher was mixed with the calculated amount of salt (NaCl) before grinding, so as to bring the mixture to the specified test. When kelp salt (see before under *Burning plants to ashes*, p. 159, method 2) was obtainable cheaply from the Scotch iodine manufacturers it was used for reducing to the specified test, because it contained 8–10 p.c. sodium carbonate.

Caustic soda ash could not be ground, as it was too deliquescent.

As the above qualities were not sufficiently pure for use in making the best qualities of glass, &c., another quality was manufactured called 'Refined white alkali.' The method was to start from an ash free from caustic soda, that is, from a sawdust carbonated ash, that had been thoroughly roasted to oxidise all oxidisable sulphur compounds, and its colour, whether yellow, brown, or grey, was of no moment, as these impurities were insoluble; without grinding this ash was dissolved in hot water in tanks provided with an immersed gauze basket for the ash, or provided with a mechanical agitator. In case the ash was not fully roasted as above 0.1 to 0.25 p.c. of bleaching powder was added during the solution to oxidise iron and sulphites, &c. The solution after settling till clear was run off from the deposited ferric oxide, sand, aluminium silicate, carbon and calcium carbonate, and entered an evaporating pan, best one arranged for fishing the monohydrate, and either top heated with special precautions or better bottom heated. The monohydrate crystals were finally dried and ignited (of course, without addition of sawdust). The product was quite white without trace of yellow tinge, and contained very few black specks; it was made largely by the Tyne Alkali Works.

The impurities above mentioned in Leblanc soda ash are the reasons why it is inconvenient or impossible to use it domestically, or for wool scouring, and for other purposes; the caustic soda, the iron, or the insoluble impurities being objectionable. For these reasons it was converted into the much purer form of soda crystals. General particulars, apart from the peculiarities of the Leblanc process, are given a little later under *Sodium carbonates, general* (see p. 179, col. 2).

Sodium carbonate decahydrate $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ has the disadvantages over anhydrous Na_2CO_3 , soda ash that for a given alkalinity it is nearly three times heavier, requires nearly three times the packages, its freight costs nearly three times as much, and it occupies in the consumers' store nearly three times as much room. But it had the advantages in the early days of the alkali manufacture that it was very much purer than the soda ash, being free from insoluble matter, free from iron, and free from caustic soda, all of which are objectionable when used for washing clothes, and that the guarantee of this purity was shown by the form of the crystals; and that when placed in a vessel of water it dissolves easily and without caking together as soda ash does. It is manufactured in enormous quantities, and is commonly known as washing crystal or washing soda.

It was not easy to convert all or nearly all the carbonate in black-ash liquor into decahydrate, or to obtain the crystals of the desired purity, or of the customary appearance; hence the most generally adopted plan was to convert the whole of the black-ash liquor into soda ash of one or more grades of purity, and such portion of it as was required as soda crystals was dissolved, clarified, and crystallised.

The quality of the soda ash required and its method of dissolving and settling was the same

as when making refined white alkali (p. 174, col. 2), except that so much care is not required in settling, as insoluble matter deposited under or on the crystals can be largely washed off.

The crystallising vessels may be either very small like hand wash-bowls, as is common in French works, or in tanks of medium size, as was the German practice, or very large up to 20 ft. by 6 ft. and 2 ft. deep, but in all cases they must be quite clean and free from rust. Crystallisation may be made to take place on iron rods hung in the vessel, as on the continent, but the practice on the Tyne, the Clyde, and Lancashire was to place several strips of sheet iron across the tank dipping slightly into the liquor, and to allow the vessel to crust over bottom, sides, and surface of the liquid. In the large tanks crystallisation is complete after 6–14 days' undisturbed cooling. A peg in a draining hole is then knocked out and the whole of the mother-liquor drained off by suitable channels to collecting tanks. The crystals are then detached and allowed to drain in the tank, or on slightly sloping tables, or are centrifuged; discoloured patches are picked out by hand. The crystals are packed in casks in this country, but in bags in France.

The liquor to be crystallised invariably contains sodium sulphate, and this is never entirely concentrated in the mother-liquor, but is found partly in the soda crystals as part of the crystals, and sometimes as separate but admixed crystals of Glauber's salt.

The general appearance of the crystals to which commerce is accustomed, large size of crystal, and a certain hardness can only be obtained if the soda crystals contain about 1 p.c. of Na_2SO_4 ; but anything much more than this is unnecessary or is a direct adulteration. The manner of the combination of the sodium sulphate with the soda crystals does not appear to have been determined, because though $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ and $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ both crystallise in monoclinic forms, yet their axial ratios and angles are very different, namely, $1.4186:1:1.4828$, $\beta = 57^\circ 40'$, and $1.1161:1:1.2382$, $\beta = 72^\circ 15'$; but perhaps they are isodimorphous, as Traube (Zeit. f. Krystallographie, 22, 143) has shown, for Na_2CO_3 and Na_2SO_3 with either $10\text{H}_2\text{O}$ or $7\text{H}_2\text{O}$, which readily form mixed crystals having the crystalline form of either of the components. Other particulars of the decahydrate not peculiar to the Leblanc process, see later under *Sodium carbonates, general* (see p. 179, col. 2).

Sodium carbonate monohydrate $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$.—The formation and use of this substance as an intermediate product in the conversion of black-ash liquor into soda ash, and especially into soda ash of increased purity, have been described under *Evaporation of black-ash liquor* (p. 171, col. 2). The compound was originally known by the name of 'black salt,' and was too impure and discoloured for commercial use. As methods of purifying the black-ash liquor (see p. 169, bottom, to p. 171) became known, the product improved so greatly in quality, that it no longer was described by its original name. In 1879 Carey, Gaskell and Hurter had still further improved the purification (see p. 171, col. 2, last par.) that by evaporation and fishing a pure white salt, sufficiently fine for commercial

purposes, was obtained and was known as 'crystal carbonate,' and had the merit of being the purest form of commercial sodium carbonate (J. Soc. Chem. Ind. 1, 26–27, and 4, 523). It was specially suitable for bleachers and dyers, and for preparing sodium bicarbonate by treatment with carbon dioxide.

For other particulars of the monohydrate not peculiar to the Leblanc process, see later under *Sodium carbonates, general* (p. 179, col. 2).

Particulars of the conversion of the Leblanc soda process to the manufacture of caustic soda are given under the heading of *Sodium hydroxide* (p. 214, col. 1, to p. 221), where the gradual disuse of the process is also described.

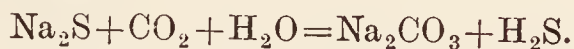
Method 9. Sodium silicate (solution) and carbon dioxide $\text{Na}_2\text{SiO}_3 + \text{CO}_2 = \text{Na}_2\text{CO}_3 + \text{SiO}_2$ was proposed in 1809 by Gay-Lussac and Thenard, and the sodium silicate was obtained by strongly heating in an atmosphere containing steam a mixture of salt and silica. This reaction was afterwards tried on a practical scale by Blanc and Bazille (1840), Fritzsche (1858) and others, especially by Gossage (1862), who brought sodium chloride in the state of vapour, along with steam, into contact with intensely heated quartz. The sodium silicate formed runs down in a fluid state. It is either used as such, or converted by CaO into NaOH , or by CO_2 into Na_2CO_3 . This process was worked for some time, but the decomposition was too incomplete, the HCl was difficult to condense, and the apparatus could not resist the intense heat.

The sodium silicate was long ago obtained from sodium sulphate by heating it and sand with coal, and so late as 1874 the St. Gobain Company for making sodium carbonate started their manufacture in this way.

The sodium silicate was also obtained in 1866 (Eng. Pat. 2026) by strongly heating sodium nitrate with silica; but the vessels employed were corroded to an enormous extent. The nitrogen oxides evolved may by treatment with water and air be converted into nitric acid.

This method has been applied to the conversion of sodium silicate in Leblanc vat liquor (p. 171, col. 1, par. (5)) into sodium carbonate.

Method 10. Sodium sulphide solution and carbon dioxide

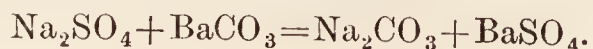


Since 1819 many persons have tried to realise this reaction, but they have not succeeded. Only by adding a considerable excess of carbonic acid could all the sulphide be destroyed, and then the alkaline product was essentially sodium bicarbonate (see p. 181, col. 1, and p. 182, col. 1).

Gossage from 1838 to 1892 made determined efforts to succeed with this process. The difficulties were: (1) the technical difficulty of making the sodium sulphide itself owing to the rapid action of fused sodium sulphide on siliceous material; (2) the fall in price of carbonate soda owing to the development and cheapening of the ammonia soda process.

Hunt, 1860, at St. Helens also failed to develop a working process.

Method 11. Sodium sulphate and barium carbonate, or strontium carbonate



This has been tried in the dry way by Kastner (1826) and Anthon (1840); in the wet way by many inventors, from Kölreuter, in 1828, to Nauhardt, in 1892 (Fr. Pat. 223339). The reaction: $\text{Na}_2\text{SO}_4 + \text{BaCO}_3 = \text{Na}_2\text{CO}_3 + \text{BaSO}_4$ is, however, incomplete, whatever temperature may be employed, even with excess of BaCO_3 .

Method 12. Decomposition by heat of sodium bicarbonate $2\text{NaHCO}_3 = \text{Na}_2\text{CO}_3 + \text{CO}_2 + \text{H}_2\text{O}$.—This is somewhat similar to the decomposition by heat of natural soda



described (p. 158, method 1). Bicarbonate for use in this method has been made by the ammonia soda process, from 1838 to the present time



for an account of which, see under *Sodium bicarbonate* (p. 182, col. 1). It has also been made from natural soda $\text{NaHCO}_3 \cdot \text{Na}_2\text{CO}_3 \cdot 2\text{H}_2\text{O}$ by dissolving and treating with CO_2 , but this process is no longer used (see p. 182, col. 1).

The ammonia soda process made but little progress from 1838 to 1860, owing to the difficulties of making the bicarbonate, but from the latter date those difficulties have been overcome and the bicarbonate has been converted into an ever-increasing output of 'ammonia soda-ash,' so that in 1895 the amount was slightly greater than the amount made by the older Leblanc process, and in 1909, in the previous edition of this work, Arthur Carey wrote that in the production of sodium carbonate the Leblanc process had been practically superseded by the ammonia soda process.

The ammonia soda process for the manufacture of soda ash is markedly different from the Leblanc process, having no corrosive gases to control, no multitudinous impurities to eliminate, no great masses of solid waste to be disposed, only the impurities in the limestone used, the only essential waste product or by-product a solution of calcium chloride, that to the water-courses is innocent compared with the waste liquors that have run from the Leblanc soda works.

The history and details of the preparation of NaHCO_3 by the ammonia soda process are found under the heading *Sodium bicarbonate* (p. 181, col. 1, to p. 193), but the details of the preparation of Na_2CO_3 from that NaHCO_3 are here given.

From the readiness with which sodium bicarbonate decomposes it would be anticipated that the roasting and furnacing operation would be an easy matter. Practically it has been found that the economical performance of this operation is one of the most difficult problems in the process. The difficulty is indicated by the large number of patents on this part of the process taken out by Solvay and others. The practice in the various works is understood to vary widely, and the details of the apparatus in actual use are, as is the case with so much of this process, kept secret.

Below are given short descriptions of some of the furnaces which have been used.

It is usual to divide the calcining operation into two stages.

In the first stage the bicarbonate is dried and the ammonia contained is driven off together

with about 75 p.c. of the second molecule of carbon dioxide, and the substance is then called 'roaster ash.' Fig. 9 represents a form of roaster which has been much used. It consists of a cast-iron pan A closed by a cover B through which passes a vertical shaft, carrying an arm with scrapers. The pan is heated by the fireplace C, and is provided with an exit pipe D, through which the gases evolved—steam, ammonia, and carbon dioxide—pass away, drawn by a pump as presently described. The pan of such a roaster varies in size from 10–14 feet.

Bradburn (J. Soc. Chem. Ind. 1896, 884) states that in the United States the form of dryer shown in Fig. 9 is in use, but is being replaced by the calciner described in U.S. Pat. 386664, 1888. This calciner consists of a cast-iron cylinder about 60 ft. long by 5 ft. diameter, supported at the ends and in the middle on roller bearings, and revolved by gear fixed in the middle. A furnace chamber is

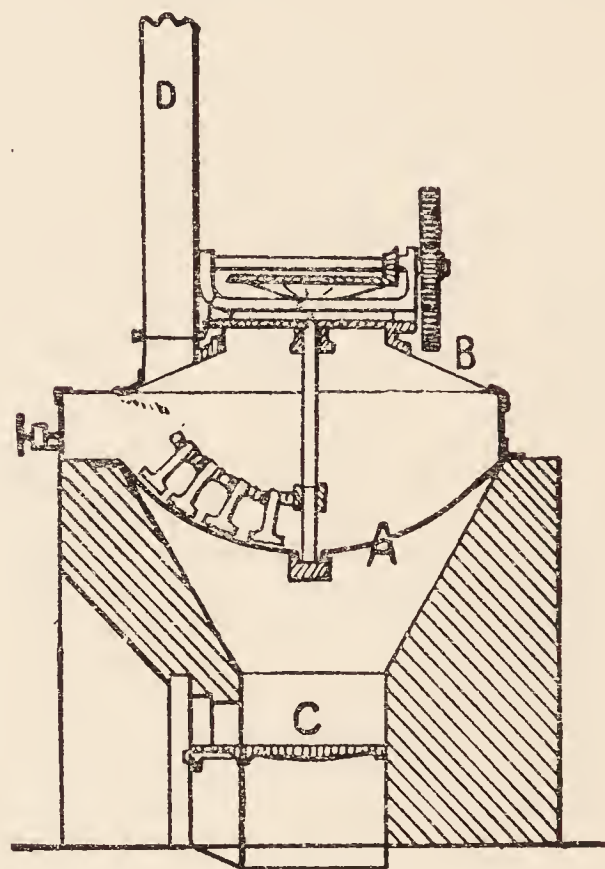


FIG. 9.

built round each half of the calciner, connected together by underground flues, so that the middle bearing and driving gear are accessible. The ash is moved slowly forward by means of a heavy chain lying along the length of the cylinder.

In the second stage the roaster ash is continuously fed into the apparatus shown by Fig. 10, known as a Thelen pan, and consisting of a cast-iron dish 7–8 ft. diameter by 30 ft. long, hooded with a sheet iron cover. The pan is heated by an external fire and rests on brick walls. The roaster ash is fed in continuously at the firing end, and slowly moved by the oscillating movement of the scrapers, which rock through an angle of about 90° , to the other end of the pan, where it is delivered to a conveyor, or to an elevator, which lifts it to the so-called cooling conveyor, usually placed in the roof of the building, and from which the ash is afterwards conveyed to the store or to the dressing and packing plant. The cooling conveyor is sometimes an atmospherically cooled revolving shell, having an inside screw fastened to the shell,

and sometimes a water-cooled conveyor (Die Chemische Industrie, 1878, 7).

The apparatus shown by Fig. 10 yields the sodium carbonate in the form of a light powdery ash requiring very little grinding before packing, but occupying, when compared with Leblanc ash, considerably more package space.

For many purposes this light, somewhat dusty ash is not liked, and a denser form has to be made by subjecting it to direct fire. When this is done the 'roaster ash,' that is the not completely decomposed bicarbonate or sesquicarbonate, taken from either the dish roaster shown in Fig. 9 or produced in a lightly fired Thelen pan, is finished in a furnace of the type of the Mactear furnace shown in Fig. 8 (p. 173), or in a rotating furnace of the type of the black-ash revolver, where the ash is brought into direct contact with the fire gases, and therefore raised to a much higher temperature than in the Thelen or other similar pan.

A 1000 c.c. jar filled and well shaken down will hold 900 to 1000 grms. of light ash, but about 1550 grms. of heavy ash.

Whatever apparatus is used for drying and

roasting the bicarbonate, arrangements are made to draw off the gases (NH_3 , CO_2 , and H_2O) evolved, by means of a pump, first through a series of water-cooled cast-iron pipes, similar to the cooler for the ammoniacal brine (see p. 188, col. 1, last par.), to cool them and to condense the bulk of the water vapour and with it a part of the ammonia. They are then usually drawn through one or more coke-packed towers, down which water is running, and in which the remainder of the ammonia is condensed as ammonium bicarbonate. The ammonia liquor both from the cooler and the scrubber is run to the store tank for ammoniacal liquor, from which the ammonia still is fed (see p. 191, col. 2, stage 5).

The gases leaving these scrubbers consist of carbon dioxide diluted by the air drawn into the roaster. Great care is taken to reduce this air leakage to a minimum, because with absolute freedom from leakage the carbon dioxide from the roaster would, of course, test 100 p.c. CO_2 , and when mixed with the lime kiln gases (see p. 185, col. 1, stage 1) pumped into the Solvay towers or carbonators would materially increase

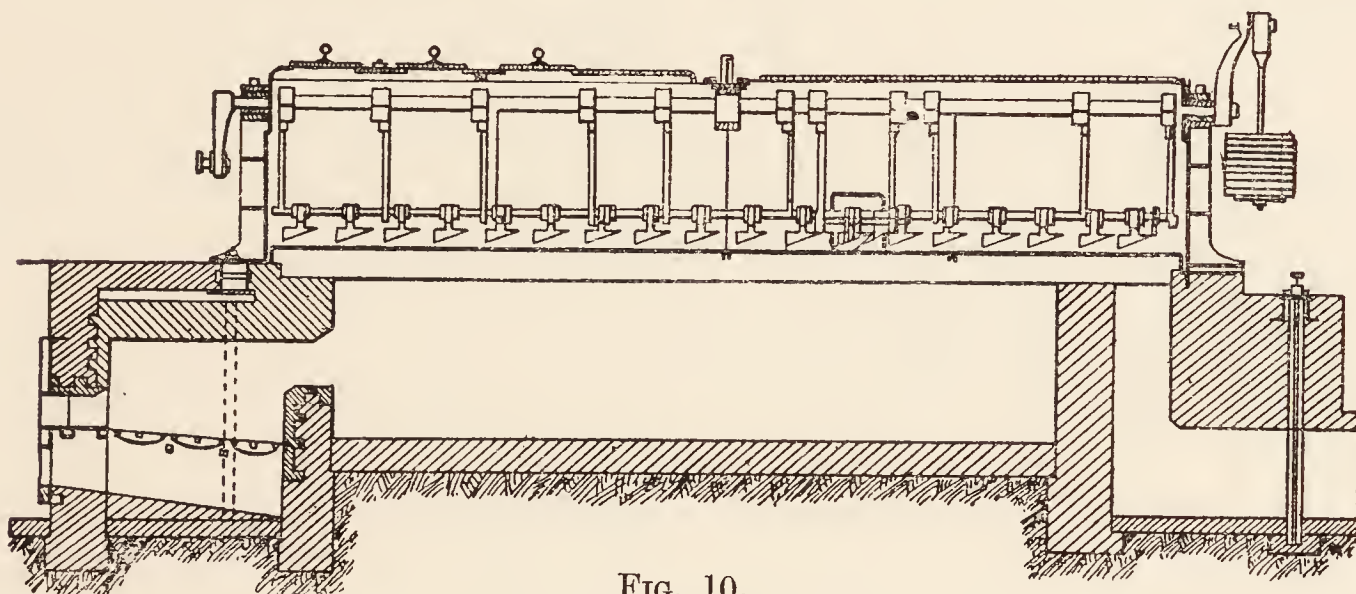


FIG. 10.

their strength. In the early days the roaster carbon dioxide tested as low as 25 p.c. With the dish roasters (Fig. 21) the carbon dioxide is stated to test about 50 p.c. With great care and the more modern roaster, such as those of the Thelen type, it is stated that a gas containing 60-80 p.c. carbon dioxide is obtained.

The finished ash has the following composition :—

Na_2CO_3	NaCl	Na_2SO_4	CaCO_3 ; MgCO_3 ; Fe_2O_3
98.00	1.20	0.12	0.40

(Bradburn, J. Soc. Chem. Ind. for 1896, 885); but it is obtained by the Brunner Mond Co. testing :

Na_2CO_3	NaCl	Na_2SO_4	CaCO_3	MgCO_3	Al_2O_3	Fe_2O_3
99.43	0.50	0.06	0.003	0.004	0.002	0.003

The use of ammonia soda ash for the preparation of caustic soda is described under *Sodium Hydroxide* (p. 220, col. 1, par. 3).

To prepare from ammonia soda ash, the decahydrate $\text{Na}_2\text{CO}_3 + 10\text{H}_2\text{O}$, 'washing soda,' the ash is dissolved in any suitable dissolver fitted with a mechanical agitator and fed with hot water. In a vessel 8 ft. diameter by 6 ft. high, 40 tons of 58 p.c. ash can be dissolved in 16 hours. The solution, made to 1.3 sp.gr. hot, is pumped

to settlers in which a small quantity of sodium sulphate is added, as commercial crystals require anything up to 1 p.c. sodium sulphate to give them the desired crystalline form (see p. 175, col. 1, pars. 3 and 4). While settling the temperature of the liquor has to be maintained above 34° , the temperature of maximum solubility. If the settlers are large and sheltered there is usually little difficulty in this. The liquor is run from the settlers into the crystallisers, which are iron vessels varying in different factories between the widest limits of shape and size. These vessels have in all cases a hole in the bottom stopped up with a long wooden plug. This hole is to permit the mother liquor from the crystallisers at the end of the crystallising operation to drain into shutes below, which convey it to collecting tanks or wells in the floor, from which it is pumped into the dissolver again to assist in making up the next batch. Across the top of the crystallisers from side to side is usually placed a number of bars or strips of metal, in order to support the crystals formed near the top of the liquor, and in this way to obtain fine large crystals. The crystallisers are usually placed in double rows, with a mother liquor shute between them, in large, airy, lattice-sided sheds. Crystallisers

yielding 1 to 1½ tons of crystals usually finish in about one week in winter and a fortnight in summer.

After the mother-liquor has been run off and the crystals allowed to drain well in the crystalliser, the crystals are taken out and may either be placed in blocks on wooden shelves to drain for at least 24 hours, after which they are ready to pack, or else they may be (for the reason next given) crushed to comparatively small pieces in a crusher frequently of the Blake type and 'whizzed' in a centrifugal machine.

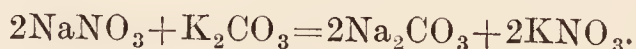
Soda crystals are either packed in wooden casks or kegs or in bags. When the casks or kegs are used it is usual to take the crystals from the draining shelf. When bags are used the better dried crystals from the centrifugal are taken, because the presence of any liquor in that case discolours the bag and the crystals.

The following is an analysis of a good brand of commercial soda crystals:—

$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$.	.	.	98.75
NaHCO_3	.	.	.	0.25
Na_2SO_4	.	.	.	0.14
NaCl	.	.	.	0.15
Water (by diff.)	.	.	.	0.71
				100.00

The mother-liquor eventually contains too much sodium chloride to be used again. It is therefore evaporated to dryness and the residue, which will contain about 29 p.c. Na_2O and 34 p.c. NaCl , is sold for what it will fetch. This necessity recurs at such long intervals that if the residue is thrown away the debit on the soda crystals made is negligible.

Method 13. Sodium nitrate and potassium carbonate



This process was known from about 1840, and was used 1854–5 during the Crimean War by Grüneberg. It has been described by several chemists, including Grüneberg (*Dingl. poly. J.* 166, 75). Later, when sugar was prepared from beetroot in quantity and the uncrystallisable residual syrup was subjected to various processes and finally incinerated, the potassium carbonate so obtained was utilised in this manner.

Method 14. Sodium bicarbonate and sodium sulphide $2\text{NaHCO}_3 + \text{Na}_2\text{S} = 2\text{Na}_2\text{CO}_3 + \text{H}_2\text{S}$.—This process was first proposed in 1840 by Wilson for making sodium carbonate. But the reaction is slow and incomplete (*see p. 181, col. 1, last par., and p. 182, col. 1, par. 2*).

Method 15. Sodium aluminate and carbon dioxide $\text{Na}_6\text{Al}_2\text{O}_6 + 3\text{CO}_2 = 3\text{Na}_2\text{CO}_3 + \text{Al}_2\text{O}_3$.—This method was first proposed in 1847 by Tilghman, who prepared the sodium aluminate from sodium sulphate and alumina by heating in the presence of steam. The decomposition of the sodium aluminate solution gave a solution of sodium carbonate, and a precipitate of alumina which was used again in subsequent operations.

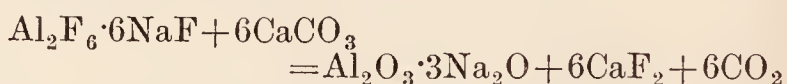
In lieu of pure alumina, the mineral bauxite, impure $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, found at Baux in the South of France, and in several other places, also at Irish Hill and Straid, County Antrim, can be

employed. Several German patents by Löwig Brothers (93 and 1650, 1877) describe this process, in which, however, the manufacture of hydrated alumina is the principal feature. A modification of the alumina process was proposed by Vogt and Figge (*D. R. P.* 31675), another by Behnke (*D. R. P.* 7256).

Ph. B. and S. P. Sadtler (*U.S. Pat.* 877376, 1908; and *Eng. Pat.* 273, 1908) decompose alkaline sulphates by heating with excess of bauxite. Peniakoff (*D. R. P.* 80063) ignites bauxite or aluminium sulphate with sodium sulphate in the presence of alkaline sulphides or pyrites to produce sodium aluminate and sulphur dioxide. Projahn (*D. R. P.* 112173; *Eng. Pat.* 6790, 1899) heats salt-cake with aluminous substances with exclusion of air, and with metallic iron at a dark red heat, and then lixiviates.

The sodium aluminate was also prepared from alumina and sodium chloride, in the presence of steam, at a very high temperature (Tilghman in 1847); and this method has been taken up more vigorously since the discovery of native alumina in the mineral bauxite. But the temperature required for the decomposition is too high, and the vessels employed cannot be made to last. On this account the subsequent attempts of Gossage (1862), of Grüneberg and Vorster (1876), and of Lieber (1878) have had no practical results.

The sodium aluminate was also prepared from cryolite (*see Vol. II. 427*) by heating it with calcium carbonate

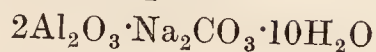


by Julius Thomsen of Copenhagen in 1849. This process has the advantage that a very pure alumina is produced as a by-product. Cryolite is found mainly in the Bay of Evigtok, South Greenland. From 1857 several factories were erected for this purpose in various parts of Europe, but since 1865 the Pennsylvania Salt Manufacturing Company at Natrona, near Pittsburg, has obtained the control of all the available mineral that is used for the process, so that no soda can be made from it elsewhere.

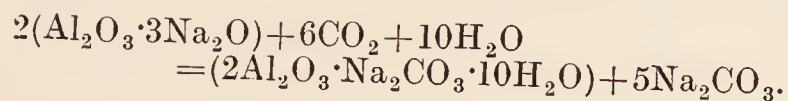
Cryolite as it comes into trade usually contains about 15 p.c. of impurities (galena, pyrites, fluorspar, calcspar); except for these impurities it is a snow-white mineral, easily fusible. Finely-ground cryolite (100 parts) is intimately mixed with 150 parts of ground chalk, and some of the impure CaF_2 obtained in the process itself is added to the mixture, which causes the cryolite to decompose more completely. The mass is spread in a thin layer, and heated to a red heat (but short of being fluxed, which would cause an imperfect decomposition) in furnaces specially devised by Thomsen for this purpose, which finish each charge of 9½ cwts. in 2 hours (*cf. Lunge's Sulphuric Acid and Alkali*, iii. p. 220). The furnace charge is put, while hot, into the lixiviating tanks, and is methodically washed. The residue from this operation is an impure calcium fluoride, which finds various uses.

The solution of sodium aluminate, 48°Tw., is decomposed in revolving cylinders, or in vessels provided with agitators, by the carbon

dioxide from a lime kiln. A white granular readily settling precipitate



is formed, and the mother-liquor contains carbonate equal to about 83 p.c. of the total alkali



The solution produced in the precipitating vessels is boiled down to 66°Tw., and on cooling yields a crop of extremely pure soda crystals, containing hardly more than $\frac{1}{4}$ p.c. of foreign salts. The mother-liquors are so pure that they can always be taken back again into the process. The precipitate of double carbonate is digested for a long time with repeated doses of hot weak solutions and hot water until it contains only 2 p.c. of soda, and the strongest of the solutions so obtained is used to dissolve fresh aluminate. The whole of the soda cannot be extracted without making the precipitate gelatinous and difficult to settle.

In 1878 the sodium aluminate was obtained by Liermann by heating a mixture of sodium sulphide and alumina in a current of hot air; sodium aluminate is formed, and the gaseous products which escape are passed into a vitriol chamber.

Method 16. Sodium sulphide, iron oxide and coal were used in 1854 by Blythe and Kopp at Church, near Manchester. The fused material cannot be successfully lixiviated at once, but it requires to stand 8 days in a chamber filled with the gases from burning coke, when the blocks fall to powder. The powder, when lixiviated, yielded good soda crystals, or by evaporation to dryness and calcining gave a soda ash containing 80–95 p.c. Na_2CO_3 . The sulphide of iron was roasted to recover SO_2 and Fe_2O_3 , both of which were used again. Much was expected of this process, even that it would supplant the Leblanc process. But the recovery of the SO_2 , which was its principal advantage over the Leblanc process, was not attained, mainly because the insoluble sulphide of iron was not FeS but $\text{Fe}_2\text{Na}_2\text{S}_3$ (Stromayer *Annalen*, 107, 233), and it had to be treated specially to recover the sodium. The original melting was also highly corrosive on fireclay and on cast iron. These and other difficulties caused this process to be abandoned.

The process appeared again in 1890, when Reynaud took out Eng. Pat. 14483. He heated NaCl with sulphide of iron to obtain chlorine gas, and a residue of sodium sulphate and ferric oxide. By adding to the residue coke all the materials for Blythe and Kopp's process just described were at hand.

Method 17. Sodium sulphide heated with barium carbonate $\text{Na}_2\text{S} + \text{BaCO}_3 = \text{Na}_2\text{CO}_3 + \text{BaS}$.—This method, proposed in 1858 by Reinard, is only a modification of Leblanc's calcium carbonate method, but there is no advantage, and the cost is much too great.

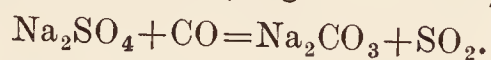
Method 18. Sodium sulphate, barium carbonate and carbon dioxide.—In 1851 Brit. Pat. 13556 showed that the very slow and imperfect reaction between sodium sulphate and barium carbonate was greatly facilitated if some carbon dioxide was added. After the work of Wagner,

Kuhlmann, Brunner, Lunge (1866) it was known that only if sufficient carbon dioxide was absorbed to convert all the sodium into bicarbonate was the reaction easy and quite complete. This process would be practicable, if a cheap method of recovering the BaCO_3 from the BaSO_4 could be found. Bramley (Eng. Pat. 1050, 1886) made efforts in this direction, but not successfully.

Method 19. Sodium bichromate and coal were proposed in 1867 by Kessler, for when heated they yield Cr_2O_3 and Na_2CO_3 . The Cr_2O_3 was to be used again for making more bichromate by Swindell's process of 1851, viz. by heating Cr_2O_3 and NaCl in the presence of air and moisture, the chlorine escaping as HCl , but as this reaction is very incomplete, Kessler's process fails.

Method 20. Sodium sulphate and calcium bicarbonate were patented in 1872 by Pongowski, in France, but Lunge (*Dingl. poly. J.* 243, 157) found that this causes no formation of sodium carbonate whatever.

Method 21. Sodium sulphate and carbon monoxide (in presence of carbon dioxide, and at a red heat), were patented in 1885 by Kayser, Young and Williams (Eng. Pat. 7355),



The process was reviewed in *Dingler's Poly. J.* 262. Watson Smith and W. B. Hart were unable to find any such reaction (*J. Soc. Chem. Ind.* 1886, 643).

It has been tried on a practical scale at the Hautmont works, in France, in an apparatus similar to that of Hargreaves and Robinson for the manufacture of sodium sulphate, as the reaction is a very slow one. The drawbacks found there were: that the mass crumbles to powder, which stops the passage of the gas; that it is very difficult to keep the temperature at the proper point; and that all the sulphur dioxide is too dilute for utilisation (Lunge, *Pariser Ausstellungsbericht*, 1889, 15).

Method 22. Sodium phenate and carbon dioxide $2\text{NaOC}_6\text{H}_5 + \text{CO}_2 = \text{Na}_2\text{CO}_3 + \text{C}_6\text{H}_5\text{OH}$.—This method was proposed by Staveley (Eng. Pat. 17657, 1887). He agitates crude phenol from coal tar with milk of lime and treats the resulting solution of calcium phenate with sodium sulphate. Calcium sulphate is precipitated; the solution of sodium phenate is decomposed by CO_2 into sodium carbonate and free phenol, which is used over again. *Cp.* also Staveley's paper, *J. Soc. Chem. Ind.* 1888, 807. This process is ingenious, but no doubt impracticable, especially owing to the hardly avoidable loss of phenol.

Sodium carbonates, general.—The historical account of the various methods of preparing sodium carbonate, or its hydrates with one or ten molecules of crystallisation water being now completed, some general details of these three substances are given that are independent of the particular method of preparation.

The commercial soda test used for trade purposes does not agree with the real percentage of Na_2O in the product. This is well known to the trade and is universally accepted under the name of the Liverpool test, or the Newcastle test. The discrepancy between real soda and the commercial test originated in the early days of

the manufacture, when the atomic weights of Na, O and C were 24, 8 and 6, and the formulæ of sodium monoxide and carbonic acid were NaO and CO₂, and accordingly the percentage of sodium monoxide in sodium carbonate was 59.26. With the modern atomic weights and formulæ, the percentage is 58.49. Pure sodium carbonate has always been used for standardising the acid used in alkalimetical tests, and the supposed variation of composition of the sodium carbonate is the cause of the variation between the old and the modern tests. The alkali maker's handbook (Lunge and Hurter, pp. 139–141) gives a table for the conversion of these tests. Further, it has been customary to record the results of alkali tests in whole percentages only, so that a decimal less than 0.5 would be quite ignored, while a decimal of 0.5 or more would be ignored but the units figure of the percentage would be increased by one unit. For the volumetric methods of determination, *see* Vol. I. 56.

The solubility of sodium carbonate in water depends largely upon the particular hydrate which is in contact with the solution if the temperature is below 35°; if the solid is Na₂CO₃·10H₂O, then the solubility in grams Na₂CO₃ per 100 grams water is at 0° 7.1, 10° 12.6, 20° 21.4, and at 30° 40.9; if the solid is Na₂CO₃·7H₂O rhombic, the solubility at the same temperatures is much greater, namely, 20.4, 26.3, 33.5 and 43.5. Above 35° only the hydrate Na₂CO₃·H₂O exists and the solubility is at 40° 49.7, 50° 47.5, 60° 46.4, 70° 45.8, 80° 45.7, 90° 45.2, 100° 45.1, and at the boiling-point 104.7° is 45.1. A solution of sodium carbonate when boiled, slowly loses CO₂ and forms NaOH, and by passing inert gases continuously notable amounts of CO₂ can be removed.

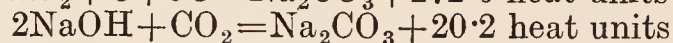
Tables of sp.gr. of sodium carbonate solutions and of the variations produced by temperature are given in Lunge, ii. 1, 50, and Lunge and Hurter, 133, and the same for solutions up to 15 p.c. are found in Landolt, Bornstein Roth, pp. 256 and 289. Sodium carbonate is only slightly soluble in strong caustic soda solutions, and can be separated from caustic soda in this way, *see* under *Sodium hydrate* (p. 213, col. 1, Freeth; p. 214, col. 1, red liquor, to p. 215; p. 217, col. 1, evaporation, to p. 219; p. 220, col. 1, losses; p. 224, col. 1, last par., to end of page).

Sodium carbonate, anhydrous, Na₂CO₃, is a white opaque powder of sp.gr. 2.476. At 852° it fuses to a colourless liquid of sp.gr. 1.9445–0.00040 (t°–900°) and rather readily parts with a small portion of CO₂, the amount of which varies with the atmosphere above the salt; if hydrogen or steam are present even 20 p.c. NaOH may be formed, if nitrogen is present 1.8 p.c. of the Na₂CO₃ is converted into Na₂O, if carbon dioxide is present and the temperature is not much above the melting point no decomposition occurs and the flux after solidifying is nearly transparent. An easy method of preparing pure Na₂CO₃ for standardising acids for volumetric analysis is to heat pure NaHCO₃ in a platinum crucible in a sand bath at 270°–280° for 20 minutes. Anhydrous Na₂CO₃ exposed to the air absorbs moisture and also CO₂ and cakes into hard masses.

When brought into contact with water it

hydrates and if not kept agitated may set like cement.

Its most important thermal data are—



Na₂CO₃ dissolved in 400 H₂O evolves 5.64 heat units.

Commercially it is known as 'soda ash' if prepared by the Leblanc process, as 'ammonia soda ash' if prepared by the Solvay ammonia processes; as 'caustic soda ash' if it contains admixed caustic soda; as 'yellow soda ash' if containing traces of iron oxide, as 'white soda ash' or 'refined soda ash' if free from iron oxide, as 'heavy soda ash' or as 'light soda ash' according to the degree of its ignition and consequent fritting and shrinking.

Applications.—For glass-making sodium carbonate is preferable to sodium sulphate, as it reacts at lower temperatures, is generally freer from iron, and evolves no injurious acid fumes. For conversion into caustic soda solution in paper and soap works. As an ingredient in soap powders, for which purpose its freedom from caustic soda is advantageous. For wool scouring, and here the absence of caustic is necessary. For a multiplicity of purposes by cotton and calico bleachers (*see* Vol. I. p. 603), and by dyers and printers. For softening boiler feed waters. For the manufacture of borax, ultramarine, sodium silicate, and in a multiplicity of chemical processes.

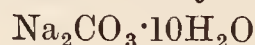
Sodium carbonate, monohydrate Na₂CO₃·H₂O, commercially known as 'crystal carbonate.' This hydrate crystallises in small rhombic crystals when a strong solution is cooled to not less than 35°, or when a solution is boiled until crystals separate.

Crystal carbonate dissolves in water very easily, because it slightly raises the temperature in the act of solution, and because its grainy texture offers a very large surface to the water.

One ton of crystal carbonate contains as much alkali as 48 cwts. of soda crystals, and occupies only 65 cubic feet against 150 cubic feet occupied by 48 cwts. of soda crystals.

Although made by the Leblanc process at first (*see* p. 171, col. 2, last par., to p. 175, col. 2), it is now made from ammonia soda ash.

Sodium carbonate, decahydrate



'soda crystals,' was obtained from Leblanc soda ash by solution, settling, and crystallisation. They were required for scouring wool and for household purposes, because the Leblanc soda ash itself was not suitable, chiefly on account of its contained caustic soda which destroys wool and skin; but it contained also sulphides and polysulphides and ferrocyanides that were also objectionable.

For all manufacturing purposes Leblanc soda crystals are now advantageously replaced by ammonia-soda, which is equally free from caustic; but for household purposes soda crystals, commonly known as 'washing soda,' are still demanded in very large quantities, and are now obtained by the ammonia-soda process with only impurities NaCl 0.18, and Na₂SO₄ 0.12 p.c.

The great effort of Leblanc crystal makers was to find out how to obtain a good crystal

from the vat or tank liquor direct, but the bulk of the crystals made (and probably all those of good quality) were produced from Leblanc ash. Soda crystals are now made from ammonia soda ash (*see* under Solvay ammonia soda process, p. 177, col. 1, last par.).

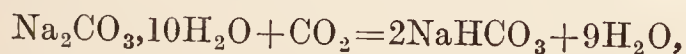
Commercial soda crystals are sometimes adulterated with Glauber's salts, specially manufactured in large crystals, and it is said that now and then Glauber's salts are vended as 'best Scotch soda,' but it is hardly credible that such an easily discoverable fraud is frequently committed.

Mactear (Eng. Pat. 10651, 1884) has constructed an apparatus for obtaining soda crystals in a granular form, by water-cooling the exterior of the crystallising vessel while continuously agitating the crystallising liquor. Eng. Pat. 1989, 1886, describes compressing those granular crystals into the shape of tablets, cakes, or blocks, most conveniently of a rectangular form, so that they can be packed without waste of space.

The crystals, sp.gr. 1.458, are often very large and the crystalline form is then readily seen; the form is monoclinic. Exposed to the air if the temperature is below 12° and the dew-point above 8.1° no change takes place, and the faces of the crystals maintain their glassy lustre; but if the temperature of the air is slightly warmer the crystals effloresce with formation of $\text{Na}_2\text{CO}_3 \cdot 5\text{H}_2\text{O}$; at 34° it melts and deposits a certain quantity of $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$.

When a strong solution is crystallising to form $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ the latent heat of solution is evolved and the temperature falls exceedingly slowly.

Sodium bicarbonate NaHCO_3 was formerly made by the action of carbonic acid (usually obtained by decomposing CaCO_3 with hydrochloric acid) on soda crystals, and for this purpose soda crystals of yellow colour or otherwise inferior quality could be utilised quite well. They were exposed to the action of the gas in apparatus of various shapes, made of brickwork, wood, or preferably of iron, holding up to 60 tons of crystals, connected in such way that the gas passed from one chamber to another. Large doors served for charging and emptying. A false bottom, made of laths, was laid down inside, below which the gas entered and above which the crystals were put so as to form a uniformly thick bed. An abundant drainage of liquor caused by nine of the ten molecules of water of crystallisation being set free:—



dissolved the small quantity of impurities contained in the crystal soda, and ran through the false bottom, and was drained away through a U-tube fixed in the chamber bottom. The end of the process was indicated by the stoppage of this flow, which generally occurred in from 6 to 9 days. On opening the chambers the bicarbonate was found apparently in the shape of the crystals originally charged, but in reality only as a loose powder. It was very damp, and had to be dried in stoves heated to a temperature not exceeding 45° for 8 to 10 days. The product contained 87–90 p.c. NaHCO_3 .

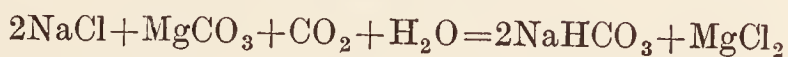
Mathieson and Hawliczek (Eng. Pat. 150,

1886) prepared pure sodium bicarbonate from black ash, crude sodium sulphide, or crude bicarbonate as obtained in the ammonia-soda process (*see* pp. 182–193), by dissolving those products in a solution of sodium chloride of from 16 to 19 p.c., and treating the solution with carbon dioxide; iron oxide, alumina, and silica are first precipitated and are filtered off; further treatment with carbon dioxide precipitates the sodium bicarbonate very pure and very completely.

Carey, Gaskell and Hürter in 1881 and 1882 (Eng. Pat. 2876, 1882) developed a method for treating 'crystal carbonate' $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ obtained by the Leblanc soda process (*see* pp. 160–175), by exposing it under a slight pressure, and in presence of a certain amount of moisture to the action of pure carbon dioxide. The reaction took place in cylinders of 8 ft. length and 5 ft. 6 ins. width, each containing a charge of 1½ tons. They were supported on hollow trunnions; gas-pipes pass through these, and upwards inside the cylinder, so that they are not stopped up by the salt which more than half filled the cylinders. The temperature rises very much during the absorption, which requires 5 or 6 hours for its completion. The bicarbonate is very pure, containing about 97 p.c. real NaHCO_3 . The patent contains also provision for employing impure carbon dioxide, by passing the gas through a series of absorbing cylinders; but this process does not seem to be in practical use. (Anhydrous monocarbonate can also be used by introducing steam together with carbonic acid.) This process had almost superseded the old process when it was itself displaced by the ammonia-soda process.

Sodium bicarbonate has been made by a process devised by Lunge (1900) from native soda $\text{NaHCO}_3 \cdot \text{Na}_2\text{CO}_3 \cdot 2\text{H}_2\text{O}$ (*see* p. 193) with the object of purifying the native soda. The crude native soda is dissolved in the soda-lake water at 80°, the solution clarified, and then treated with CO_2 obtained from a later stage; this causes the deposition of pure NaHCO_3 , and the mother-liquor contains the impurities NaCl , Na_2SO_4 , &c. This bicarbonate is heated in Thelen pans to obtain (1) CO_2 as described above, and (2) pure soda ash (*see Sodium Carbonate* p. 176), Lunge, ii. 1, 62.

W. Weldon patented (March 1, 1866) a process founded on the reaction:



but it is far too incomplete for practical use.

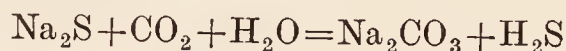
Peniakoff (Fr. Pat. 405611, 1908) concentrates the impure liquors containing sodium carbonate, which are obtained in making pure alumina from bauxite (*see* p. 178, col. 1, par. 10) to about 1.3 sp.gr., and then treats them with carbon dioxide, which precipitates sodium bicarbonate.

Ammonium carbonates have been several times proposed for decomposing Na_2SO_4 , first by Bower (1840). After the analogous process with NaCl , Solvay's Ammonia Soda Process (*see* p. 176) had attained such complete success, the above has been again proposed, principally in order to recover the chlorine, as well as the soda, by interposing the manufacture of sodium sulphate and hydrogen chloride.

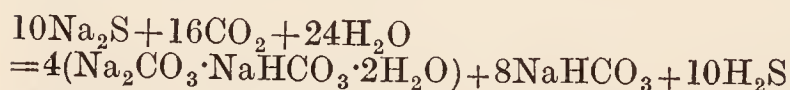
Calcium hydrosulphide is employed by

Haddock and Leith (p. 169, also by Simpson (Eng. Pat. 17765, 1890) in the following way: Saltcake, nitre-cake, or the like are converted by $\text{Ca}(\text{SH})_2$ into CaSO_4 and NaHS ; this is carried on in closed vessels under a pressure of 60–80 lbs. per square inch. The clear liquor is decomposed by CO_2 , and the H_2S set free is passed into milk of lime, in order to re-form the original calcium hydrosulphide; the soda is precipitated as NaHCO_3 .

In 1819 Atwood obtained an English patent for the decomposition of Na_2S by CO_2 , to produce sodium carbonate, Na_2CO_3 ; but the desired reaction

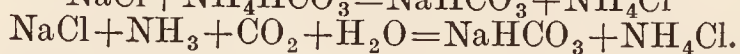
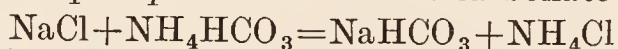


was so far from complete that the process could not be realised. Since that date Gossage (1838), Hunt (1861), Theissig, Verstract and Oliver, Claus Gomeg, Weldon, have tried to develop this process, but in doing so it changed from a process to produce sodium carbonate to a process for producing sodium bicarbonate, since on passing more carbon dioxide the remnants of the Na_2S are decomposed but the reaction is then

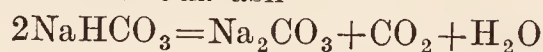


Mathieson and Hawliczek (1886) suggested the use of a brine solution instead of water to dissolve the Na_2S in order to take advantage of the lower solubility of NaHCO_3 in brine than in water. Thompson (1887), Chance (1888), Parnell and Simpson (1888), Gossage and Williamson (1888), have also tried to develop the process.

The ammonia soda process.—Strong brine treated with ammonium bicarbonate, or with ammonia and carbon dioxide gases gives a granular precipitate of sodium bicarbonate



Although the product of this reaction is sodium bicarbonate, the obtaining of this substance was not the ultimate object of those who developed this process, for as soon as they had isolated it they promptly decomposed it by heat to obtain soda ash



for which soda ash there were a great number of uses and an enormous demand. The first germ of this process, which has quite revolutionised the alkali trade, originated in various quarters. A German chemist, Vogel, is said to have known the reaction as early as 1822, and a Scotch chemist, John Thom, seems to have actually made some soda, in a crude way, by that process in 1836. Mond (J. Soc. Chem. Ind. 1885, 527) has definitely disposed of the attempt made by several French *savants* to claim the merit of the invention of this process for their countrymen, Schloesing and Rolland. Quite recently a claim has been set up for Fresnel, who is said to have made soda from common salt and ammonium carbonate in 1811, according to some hints found in recently-discovered private letters; evidently he did not meet with much success, as nothing came of his attempts. It is beyond doubt that the real history of the ammonia soda process dates from June 30, 1838, on which day Harrison Grey

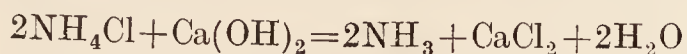
Dyar and John Hemming, both chemists residing in London, patented a process embodying all the principal reactions now carried out. This was done even more clearly in an additional patent, taken out in France on May 18, 1840, on their behalf, by Delaunay, where the use of a current of carbonic acid is first mentioned. A number of patents by other inventors followed, among which that of Gossage (1852) is remarkable, and those of Schloesing and Rolland (1854 and 1858) have become best known by the detailed description they gave in Ann. Chim. 1868, 64, 1, of their process. Although their apparatus was very ingenious, it must have been deficient in important portions, for they could not make their works pay, and the reasons given for their abandoning the process are quite inconclusive. In many other places works had been erected for making ammonia soda: by Dyar and Hemming, in Whitechapel; by Muspratt, at Newton; by Gossage and Deacon, at Widnes; and by a number of French and German manufacturers. But although we find every feature of the now-successful processes in these older establishments, there was always something wanting, and especially the recovery of ammonia seems to have been too incomplete, so that at that time the ammonia soda could not compete with the Leblanc soda even in localities where the loss of the hydrochloric acid would not have been of much consequence at that time. Apparently, about 1860, nobody manufactured ammonia soda, and the failure of all previous attempts in that direction had evidently discouraged nearly all chemists.

It was reserved to Ernest Solvay, of Brussels, to find the solution of that long-pursued problem. His first patent dates from 1861, but the process as we know it now is first described in his English patent of September 12, 1863, followed by many others in 1872, 1876, 1879, and later on. His works at Couillet, in Belgium, were started in 1863, and soda made there was exhibited in Paris in 1867 without exciting much attention. But since 1872 his triumph was assured, and has given rise to a host of other inventions, most of which have again passed into oblivion, while a few have stood the test of practice, so that ammonia soda is now manufactured not merely by Solvay's processes (which certainly furnish the largest share), but by several other independent and partly secret processes.

In 1872 the Solvay patents were introduced to Northwich by Ludwig Mond, and in 1874 Brunner, Mond & Co. started to use natural brine in place of rock salt, and various improvements enabled them to build up a powerful works. The process was also started in the United States.

The manufacture of soda ash from the sodium carbonate produced by the process grew constantly, in 1895 it slightly exceeded that made by the Leblanc process, and in the previous edition of this work, 1909, A. Carey wrote that in the production of sodium carbonate the Leblanc process had been practically superseded by the ammonia soda process. The Solvay process has in latter years manufactured many other chemicals than soda ash, namely, pure sodium bicarbonate, soda crystals, sodium sesquicarbonate, crystal carbonate ($\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$) and caustic soda.

The ammonium chloride produced in the ammonia soda process was always heated with lime

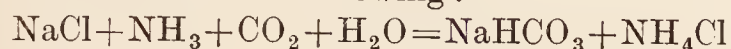


to recover the ammonia for use again in the process. The calcium chloride, previously waste, is now partly recovered, and used for laying the dust on roads, and as circulating liquor in low temperature installations, and is partly used for treating zinc carbonate ores and so preparing crude zinc chloride solution, from which cadmium was extracted, and lastly by electrolysis gave the purest zinc and bleaching powder.

The latest prospect of the ammonia soda process is named by F. E. Hamer in *Met. & Chem. Eng.* 1920, 23, 22, namely, to utilise synthetic ammonia and its residual carbonic acid gas to produce soda ash and ammonium chloride, and this last is to be used for agricultural purposes; see also *Applied Chem. Reports*, 1920, 70, 163, and *J. Soc. Chem. Ind.* 1920, 209 R.

The details of that part of the process which relate to the manufacture of sodium bicarbonate will now be described, while the details of the conversion of the bicarbonate into sodium carbonate are described under the head of *Sodium carbonate* (see p. 176, col. 1, method 12, to p. 178).

The reaction on which the bicarbonate process is based is the following:

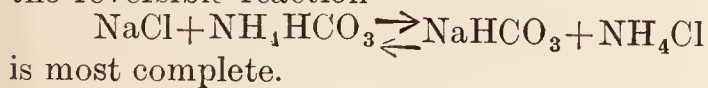


that is, sodium chloride solution is treated by ammonia and by carbonic acid. If this treatment takes place at a low temperature, it leads to the precipitation of sodium bicarbonate, this salt being sparingly soluble in a solution of ammonium chloride. The mother-liquor, containing ammonium chloride, is treated with caustic lime, and the ammonia is thus recovered, calcium chloride remaining behind as a waste, but inoffensive, product.

Simple as this statement appears, a great amount of research has been devoted to working out the theory of the reactions.

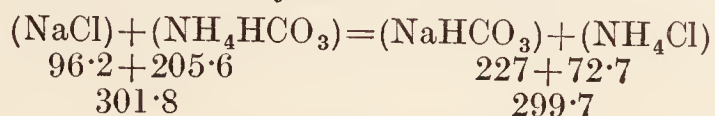
From the nature of the case much of this work has not been made generally known, and is not, therefore, available, but the following names and references indicate a large part of what has been published. Alex. Bauer, *Ber.* 1874, 292; Grünsburg, *ibid.* 1874, 644; Honigman, quoted by Landolt in *A. W. Hofmann's Vienna Exhibition Report*, 1875, 1, 452; Schreib, *Zeitsch. angew. Chem.* 1888, 283; 1889, 445, 485; Bodländer and Bruell, *ibid.* 1901, 381, 405; M'Coy, *Amer. Chem. J.* 1903, 29, 437; Hs. Jüptner, *Oest. Chem. Zeit.* 1904, 247; Fedotieft, *Zeitsch. physikal. Chem.* 1904, 49, 2; *Oest. Chem. Zeit.* 67; Jäneske, *Zeitsch. angew. Chem.* 1907, 1559; Meyerhoffer, *Verh. Gewerbst.* 1905, 167; Colson, *J. Soc. Chem. Ind.* 1910, 186).

The work done has practically all been from the point of view of the physical chemist, and consists in attempts partly experimental and partly in purely theoretical applications of the 'Phase Rule,' to determine the conditions of concentration and of temperature under which the reversible reaction



These conditions are in practice liable to modification from the practical necessity of obtaining the precipitate of sodium bicarbonate in such physical condition that it leaves the carbonators readily and can be efficiently washed.

The central reaction of the ammonia soda process is thermally almost a balance



The equation represents, therefore, a typical case of a reversible reaction, and the amount of change of sodium chloride into sodium bicarbonate depends on the relative quantities or active masses of the four salts. For instance, Bradburn (*J. Soc. Chem. Ind.* 1896, 882) took a sample of 'Tower liquor' filled with suspended sodium bicarbonate, and blew air at 21°C. through it for 10 hours, when the sodium bicarbonate had been completely reconverted into sodium chloride by the ammonium chloride in the liquor, and the ammonium carbonate formed had been carried away by the air. This demonstrates the importance of the presence of excess of ammonium carbonate to protect by 'mass' action the sodium bicarbonate from decomposition by ammonium chloride, and also the disadvantage of employing carbon dioxide containing undue amounts of other gases.

Another determining factor in directing the course of interaction between the four salts NaCl, NH₄HCO₃, NaHCO₃, and NH₄Cl, is temperature. A moderate reduction of temperature, by favouring the precipitation of sodium bicarbonate, and therefore its removal from reaction, increases, in accordance with the theory of mass action, the formation of sodium bicarbonate. The situation is, however, complicated by the phenomenon that by too great a reduction in temperature ammonium bicarbonate is thrown down with the sodium bicarbonate. Too low a temperature produces an unfavourable physical condition of the sodium bicarbonate precipitate, which makes the subsequent washing process in extreme cases practically unworkable. A rise of temperature increases the volatility of the ammonium bicarbonate and reduces the production of the sodium bicarbonate.

The effect of increasing the amount of water is to increase the amount of sodium bicarbonate kept permanently in solution, because sodium bicarbonate is increasingly soluble in brines of decreasing weakness (see Freeth, *Phil. Trans. Royal Soc. London*, 1922, A. 223, pp. 70-74).

The general nature of the ammonia soda process, and such theoretical considerations as are given above, are well known, and have been public knowledge for a considerable time. The actual working conditions in the successful ammonia soda works have, however, been kept to a large extent secret. A great number of patents, almost entirely for apparatus, have been taken out, but which are actually used, and with what modifications on the patent specification description, it is impossible to say.

Generally speaking, success in this process depends (subject to careful working in accordance with the theory of the reaction outlined above) on absolute regularity in work, and on the perfection of, and accurate interworking of

the mechanical arrangements used for the different stages of the process.

It is the development of the mechanical and apparatus side of the ammonia soda process which converted the failure of the pioneers and of the older workers of the process into the success of to-day's great industry.

We give below, as far as is public knowledge, the working details and apparatus used.

The raw materials required are, salt (NaCl), limestone, ammonia, and fuel.

Salt.—From the considerations detailed above it is clear that more than the theoretical quantity of sodium chloride is required. The actual excess of sodium chloride over that theoretically equivalent to the sodium carbonate produced is 30–40 p.c. The chief factories for producing ammonia alkali have been established on sites where the factory can pump its own salt as a saturated brine from salt beds in its neighbourhood, or can receive its supplies of brine through a pipe line.

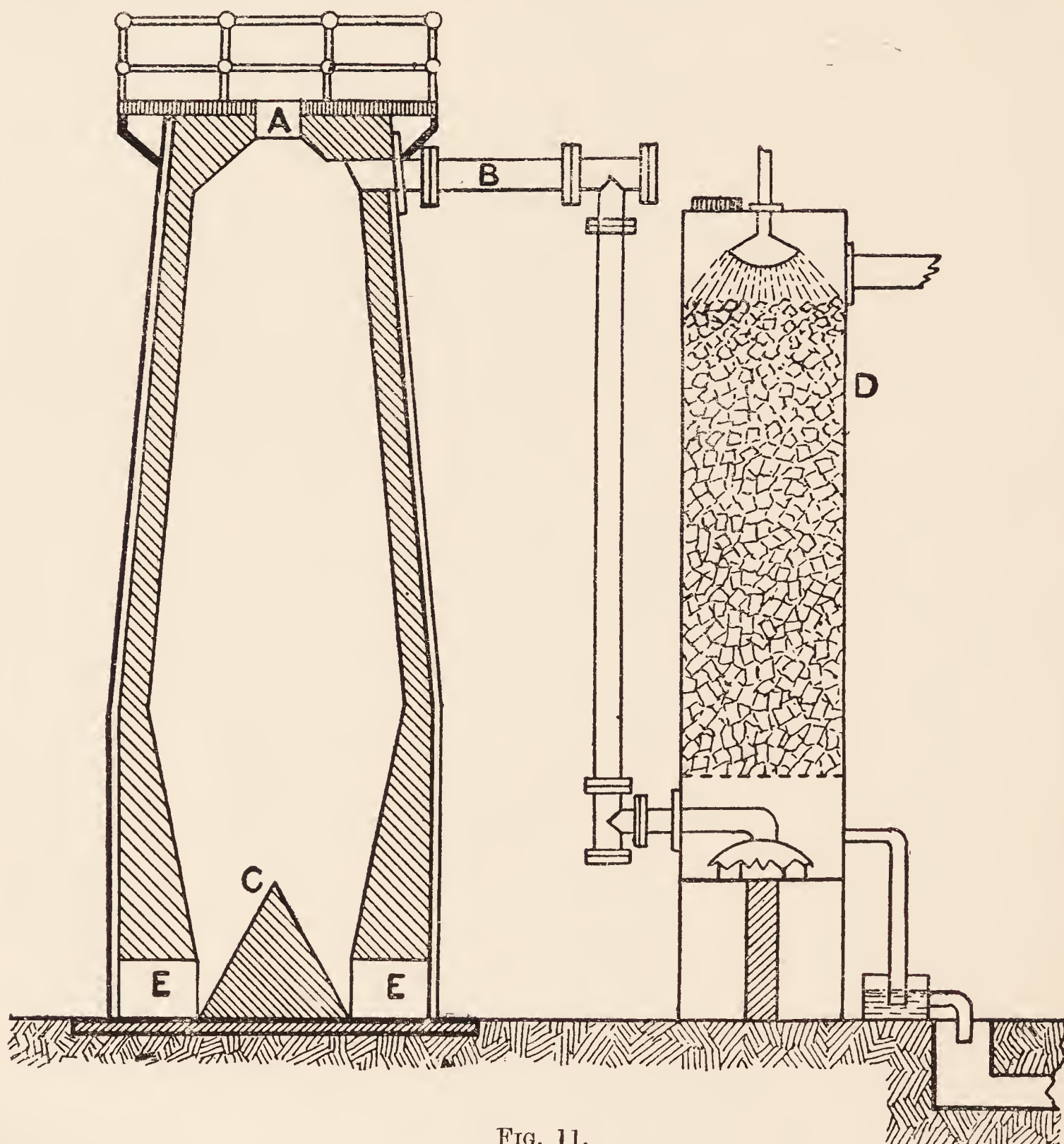


FIG. 11.

When the brine is pumped direct by the factory itself the actual cost per ton of salt so raised may be as low as 6*d.* per ton (*see* Lunge, *Sulphuric Acid and Alkali*, iii. 35). Rock salt cannot be obtained at anything like this price, and manufactured salt is still more expensive, but either may be used in small quantity to give the required strength to a slightly weak natural brine.

Brines vary in composition within wide limits, but a good brine for the ammonia soda process should contain as little as possible of lime and magnesia, and of these the magnesia is the more

troublesome. Bradburn gives the following analyses :—

	A good brine. Grms. per litre	Cheshire brine. Grms. per litre	New York brine. Grms. per litre
NaCl . . .	298·0	295·0	298·0
CaSO ₄ . . .	4·0	5·0	4·4
CaCl ₂ . . .	1·0	0·93	2·35
MgCl ₂ . . .	0·3	2·6	0·65

Limestone.—The quantity of limestone used by the process is in considerable excess of that theoretically required and amounts to 11–14 cwts. per ton of bicarbonate. It is therefore of considerable importance that the ammonia soda factory should, if possible, be within a short distance of quarries of a clean limestone free from clay and low in magnesium carbonate.

Ammonia is generally obtained in the cheapest form of ammoniacal liquor from gas works, or recovery coke ovens; these liquors contain ammonium hydroxide, ammonium carbonate, ammonium sulphide, and also tarry matters: the method of treating them is described later. The amount of ammonia required to charge a plant that produces 160 tons per day of bicarbonate is equivalent to 200 tons ammonium sulphate. The amount of additional ammonia required daily for the same plant is less than 2 tons, and may be as low as $\frac{1}{2}$ a ton of ammonium sulphate, but these low figures have only been made possible by the gradual accumulation of experience and by the better designing of the apparatus.

Stage 1. The manufacture of caustic lime and of carbonic acid gas.—This differs in details from the ordinary burning of limestone to produce quicklime only: $\text{CaCO}_3 = \text{CaO} + \text{CO}_2$. The limestone is invariably burnt by heating with coke in tall vertical kilns. The limestone, usually broken into comparatively small pieces, together with the necessary quantity of coke, is charged into the top of the kiln, and the burnt lime is drawn out from the bottom.

Figs. 11 and 12 represent types of lime kilns. These are usually 30–40 ft. high and 7–10 ft. diameter.

In Fig. 11, A is the charging hole through which the limestone and coke are dropped into the kiln. The evenness with which the comparatively small quantity of coke is mixed with the larger quantity of limestone plays a very important part in determining the extent to which the quantity of coke can be reduced, and the strength of the carbon dioxide obtainable in the gases as described later. The burnt lime is drawn out through a number of openings at the base of the kiln, of which E, E are two, and through which the air required for the combustion of the coke enters the kiln. C is a brickwork cone called a 'dumpling,' which serves to prevent the accumulation of dust in the centre of the kiln, where it could not be got at for removal, and which assists in the distribution of the air to the centre of the kiln. B is the gas exit pipe connecting the kiln to the coke packed scrubber D, of which there are usually at least two in series to each lime kiln.

Fig. 12 represents another type of kiln in which the charge is usually supported by iron bars at A, and from which the burnt lime is allowed to fall from time to time either on to the ground or into a bogie placed underneath to receive it.

According to Lunge such kilns as those described will burn 200–300 tons of limestone a week.

The important point is to obtain as high a percentage of carbon dioxide in the gases leaving the kiln as possible.

The percentage of carbon dioxide depends on the quantity of coke used, because the

chemically pure carbon dioxide evolved by the limestone on heating is mixed with the products of combustion from the coke, which cannot possibly contain more than 20·8 p.c. carbon dioxide. Hence the smaller the quantity of coke the higher the strength of the kiln gas. The following figures, calculated on the assumptions that the limestone is completely burnt and that the gases contain no small quantities

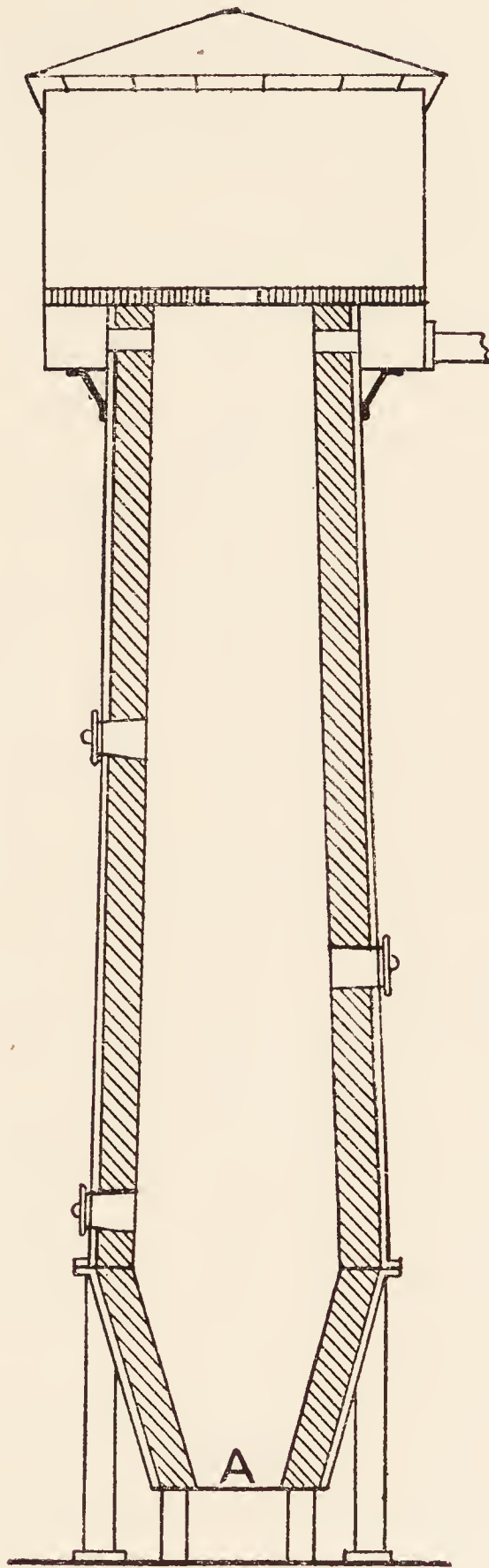


FIG. 12.

of oxygen or carbon monoxide, show approximately the relation between the coke used and the percentage of carbon dioxide.

Kiln gas strength	Cwts. coke per ton lime
31 p.c. . . .	6 cwts. coke
35 p.c. . . .	4·5 „ „
40 p.c. . . .	3·0 „ „

The kiln is worked as far as possible on the regenerative principle. The cold air entering the bottom of the kiln is heated by the burnt

lime as it drops from the zone of maximum temperature to the bottom of the kiln, and the hot gases, as they rise above the combustion zone, yield their heat to the cold limestone and coke freshly charged into the top of the kiln. Radiation losses are kept within reasonable limits by the thickness and construction of the kiln walls, and are materially reduced, of course, by a high speed of work.

The figures published for the strength of the carbon dioxide obtained in various factories vary within wide limits. Chance (*J. Soc. Chem. Ind.*) gives for good work an average test of 30 p.c. carbon dioxide. Jurisch in *Chemische Industrie*, 1910, 392, gives the average strength as 30–31 p.c. Again in other factories for many years an average strength of 32–33 p.c. has been obtained. Lunge describes in *Sulphuric Acid and Alkali*, vol. iii. 65, the Khern lime kiln, improved by Faber, which is much used in the German sugar works (*Centr. für Zucker fabr.* 1901, 532), and is stated to require 5 to 7 p.c. only of coke on the weight of limestone, and to give a gas containing 40 p.c. carbon dioxide.

The lime kiln gases after leaving the lime kiln require to be cooled and well scrubbed to remove dust, tarry material, and sulphurous acid, as completely as possible.

A common form of scrubbing plant is two or more coke-packed wrought- or cast-iron towers, about 30 ft. high by 5–8 ft. diameter, connected in series; a stream of water is run down each tower.

The lime drawn from the bottom of the kilns should be well burnt. Whatever calcium carbonate is left unburnt is, however, recovered in the lime pot, and is returned and charged a second time into the kiln with the fresh limestone. A factory producing 500 tons ammonia soda a week would require three such kilns as those described.

Stage 2. The production of ammoniacal brine.—The lime and magnesia salts which are universally present in brine have been found to be a source of trouble in the pipes and connections. In practically all cases now the brine is freed from these bases by a special process. The purification has been done as a separate process by the addition of sodium carbonate and lime, but that is not the general practice. Occasionally the soda crusts from the cleaning of the towers and sweeping of dirty soda from the floors are used.

As a rule the purification is done by the ammonium carbonate in the ammonia used for ammoniating the brine, and the scales produced by the hard crystalline magnesium salts are mechanically cleaned from the pipes and connections at intervals.

The fresh brine entering the works goes into a vessel called a tower washer, where it serves to scrub the ammonium carbonate carried over by the escaping gases from a battery of Solvay towers (*see p. 188, col. 2, stage 3, to p. 189*).

A common type of tower washer is shown in Fig. 13. It consists of a series of cast-iron rings *a, a*, divided by plates with central holes *b, b*, covered with a cup or mushroom *c, c*, which has serrated edges and often is perforated with small holes. The brine running down the tower accumulates on each plate until it is sufficiently deep to run down the

overflow pipe *d, d*, to the shelf below, where the lower ends of the pipes dip deep into the layer of brine so as to prevent any gas from passing upwards through pipes *d*. The gases travelling upwards pass through the central hole of each shelf under the mushroom, and then bubble out round the serrated edge through the brine. The fresh brine entering the top of the tower naturally meets the gases from which the ammonia has practically all been absorbed. This system of bringing gases and liquids into the most intimate contact a considerable number of times while they are travelling in opposite directions is largely used in the Solvay ammonia

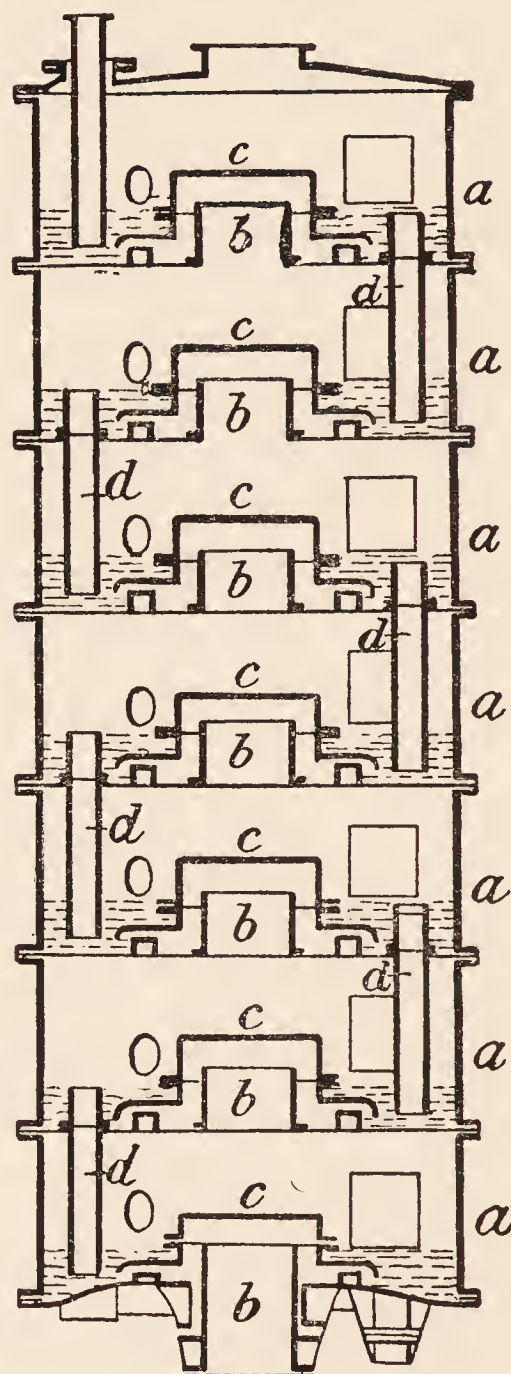


FIG. 13.

process. The lime in the brine is to a large extent precipitated in the tower washer by the ammonium carbonate absorbed. The calcium carbonate does not, however, settle out, but remains in suspension in the liquor agitated by the current of gas and travels on with the brine through the ammonia absorber or ammoniating vat to the vats or store tanks where it settles out, and in consequence the tower washer runs for many months without any necessity for cleaning.

From the tower washer the brine runs into the ammonia absorber. Fig. 14, or the ammoniating vat, Fig. 15, in either of which the brine is saturated with ammonia from the stills (*see p. 191, col. 2, stage 5*).

The ammonia absorber, Fig. 14, is made up of

a number of cast-iron rings similar in principle to the tower washer just described; *a*, *a* are the shelves; *b*, *b* mushrooms; *c*, *c* the pipes through which the liquor overflows from each shelf to the one below. They differ from those

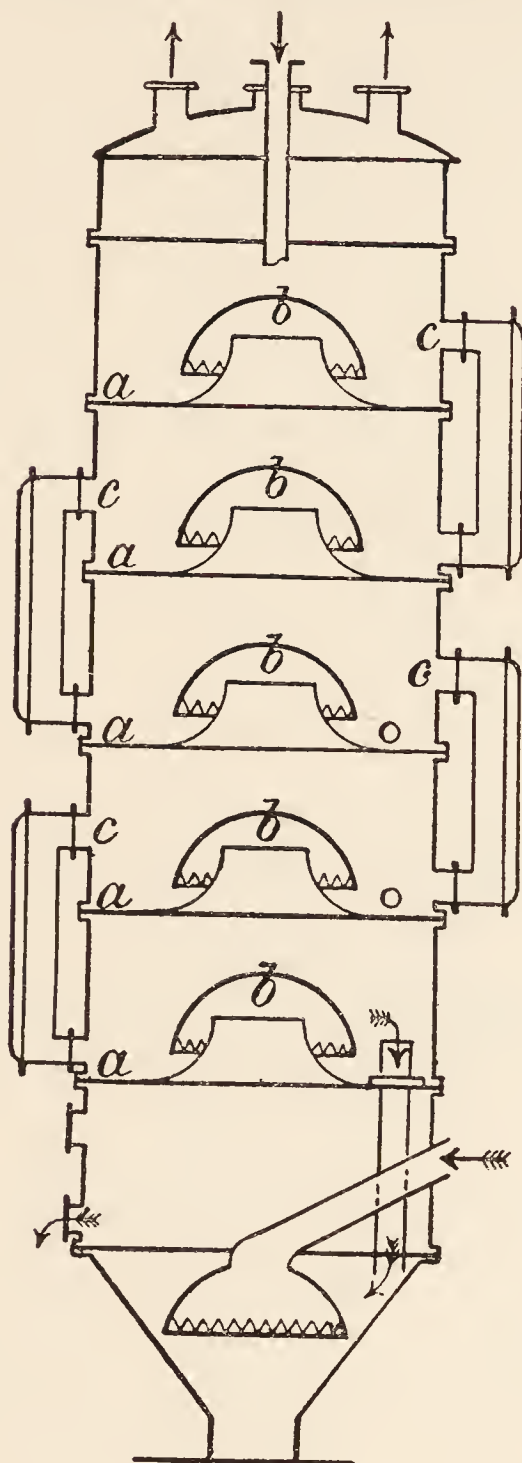


FIG. 14.

shown in Fig. 13 by being made external to the tower so as to facilitate cleaning. The bottom of the absorber is conical and the point of the cone is fitted with a discharge pipe and tap through which the sludge that settles out may from time to time be drawn.

Another type of absorber, the ammoniating vat, is shown in Fig. 15, and is a vessel built up of several cast-iron rings, frequently about 8 ft. diameter, but without the shelves shown in Fig. 14. In this case the gases enter by the pipe A, and are distributed by the single attached mushroom B. The bottom of the vessel is conical to permit the occasional blowing off of slurry. The ammoniacal gases from the stills are drawn through the absorber by a vacuum pump, which, as a check on ammonia escape, sends on the gases it has exhausted through an additional small tower or washer generally called the vat washer. The vat washer usually receives the brine coming from the tower washer and discharges it into the ammoniating vat.

Heat is generated in considerable quantities

in the absorber by the solution of ammonia, so that cooling is necessary. This is done either by an external spraying with water or preferably by internal cooling pipes, until the temperature does not exceed 30°C .

The gases entering the absorbers from the stills should be maintained at about 70° in order to prevent blockages of the ammonia main by the formation of crystals of ammonium carbonate and of carbamide (see p. 191, col. 2). As a direct consequence of this high temperature of the gases, a considerable quantity of aqueous vapour is also carried into the ammoniating vessels, and being there for the most part condensed, dilutes the ammoniated brine.

It was formerly the custom to make good this dilution by the addition of solid sodium chloride in the carbonating tower itself, this, however, is generally discontinued. If it is necessary to strengthen the cooled ammoniated brine, this is done by passing through a separate

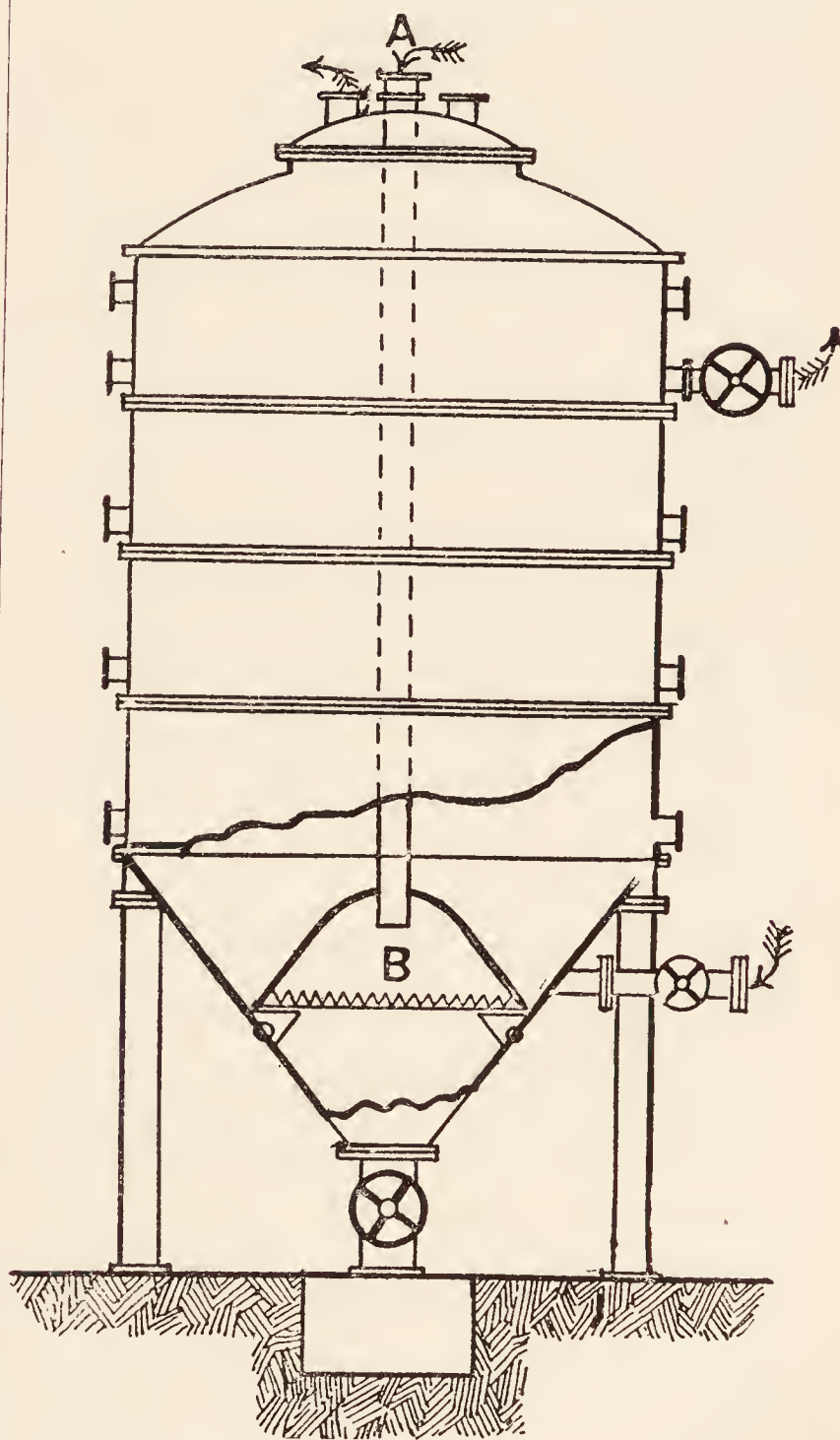


FIG. 15.

closed vessel containing salt on its way from the coolers to the carbonating towers.

A normally saturated ammoniacal brine should contain 27-28 p.c. sodium chloride and 6-7.5 p.c. ammonia. The theoretical equivalent of 27 sodium chloride is 7.8 ammonia, so that nearly equal equivalents are used, and under

this condition and on the large scale 73–78 p.c. of the NaCl is converted into bicarbonate.

The presence of ammonia decreases the solubility of sodium chloride in water. Lunge gives the following figures for the solubility of sodium chloride in water in the presence of ammonia at 15°.

P.c. NH ₃ by vol.	P.c. NaCl by vol.	P.c. NH ₃ by vol.	P.c. NaCl by vol.
—	31.8	7.0	27.4
3.5	29.5	7.5	27.1
5.0	28.6	8.0	26.8
6.0	28.0	10.0	25.4
6.5	27.7	12.0	24.1

The volume of a brine solution on addition of the 6–7½ p.c. ammonia required for the carbonation process increases by 9 p.c.

The ammoniacal brine runs in a continuous stream into the 'vats,' for the purpose of settling out the precipitated calcium carbonate. The settling vats are frequently cast-iron vessels built up in four rings on a cone-shaped bottom piece supported on columns exactly similar to the vessel shown in Fig. 15 without the gas delivery pipe A and mushroom B. A common arrangement is for the ammoniacal brine to run in a continuous stream through two of these vessels in series and from there into one or other of two more similar vessels which act as measuring tanks, one being emptied while the other is filling. The mud, consisting chiefly of calcium carbonate mixed with a considerable proportion of ferrous carbonate and hydrate, settles out mainly in the two leading vats and is drawn off through the discharge pipes at the bottom of the cones at regular intervals. A further but smaller quantity of mud settles out in the measuring vats.

The mud is usually mixed with other liquors (from the filters, for instance), and pumped to the ammonia stills where the ammonia (carried by the liquid in the mud) is recovered.

The 'tower washer,' ammoniating plant, and settling vats are usually erected at such heights that the brine will flow by gravity through the whole series. In this way the brine is only pumped once.

The absorber, vats and ammonia still are usually all included in the same vacuum circuit, the exhaust gases from which pass through the vat washer or final small scrubber mentioned above to ensure recovery of all ammonia.

The well-settled ammoniacal brine has now to be cooled as far as possible before being carbonated, and this is generally done in a series of 6-inch cast-iron pipes arranged in tiers one above the other. The pipes are either submerged in a water tank or cooled by a stream of cold water flowing down and over them. The coolers are arranged in pairs or trios so as to permit of cutting out a cooler for cleaning. For instance, if there is a set of three coolers, two of them will at any time be working, the third will be disconnected for cleaning. Very troublesome crusts are formed in these coolers, which have first to be steamed to soften them and then have to be chipped out. Reinitzer (Zeitsch. angew. Chem. 1893, 446) gives the composition of these crusts as MgCO₃, Na₂CO₃, NaCl. Pennoch (Chem. Trade Journal, 1893, 191) found crusts in the coolers of the composition MgCO₃, Na₂CO₃.

Stage 3. The carbonation of ammoniacal brine to produce sodium bicarbonate.—In the great majority of the ammonia soda works the central reaction of the process, viz. the carbonation of the settled cooled ammoniated brine, is carried out in a tower originally designed by Solvay (patented in 1872), and which is therefore called the 'Solvay Tower.'

Fig. 16 represents a Solvay tower, which

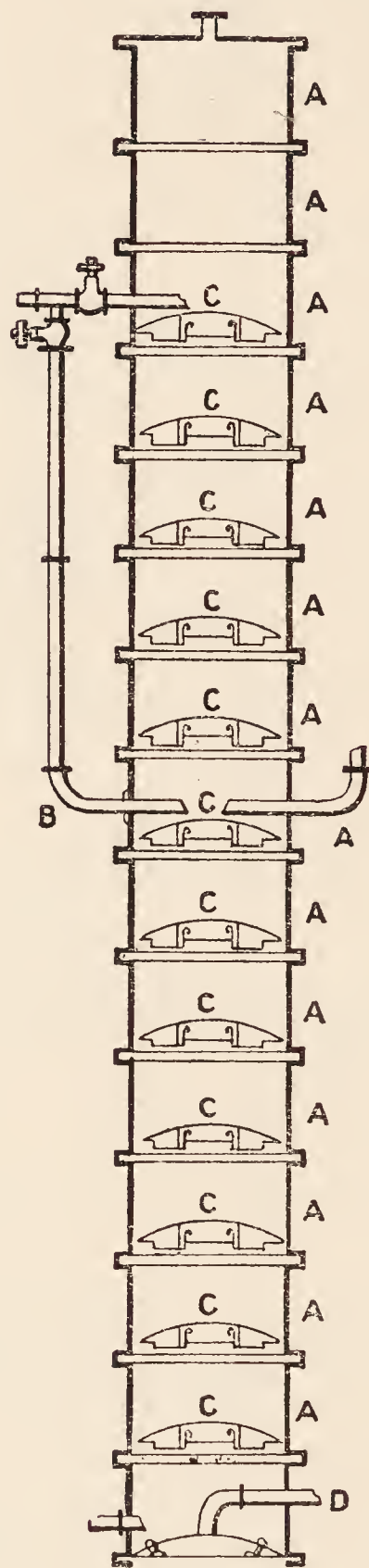


FIG. 16.

consists of a number of cast-iron cylinders, A, A, approximately 3 ft. 4 ins. deep by 5 ft. to 8 ft. diameter. The bottom of each cylinder is formed by a cast-iron disc, which (with the exception of the lowest disc) is provided with a central opening (not shown in Fig. 16, but shown in Fig. 17) about 1 ft. 4 ins. diameter. Over each opening is supported a perforated cover C (shown in detail, Fig. 17, but the other parts of this figure differ from Fig. 16, and they are described, p. 189, col. 2, Cogswell), about 6 inches less in diameter than the cylinder

itself. The number of these cylinders in a tower varies from 15 to 25.

The ammoniated brine enters the tower by the pipe B under pressure, and is maintained at a level 6 ft. to 10 ft. from the top of the tower. The object of feeding the fresh liquor part way down the tower, to which Solvay attaches great importance, is to avoid excessive volatilisation of ammonia.

The carbon dioxide gases from the lime kiln, enriched, as will be described later (*see* p. 176, method 12, to p. 178), by the carbon dioxide obtained from the first roasting of the bicarbonate, are compressed to sufficient pressure (varying with the height of the towers from $1\frac{1}{2}$ to $2\frac{1}{2}$ atmospheres) to overcome the resistance of the Solvay tower and the subsequent washers, and enter the tower through the pipe D. A constant feed of ammoniated brine is pumped into the tower at B, and a constant stream of carbon dioxide is pumped into the bottom of the tower at D.

The gases travelling up through the openings in the bottom plates of the cylinders are subdivided by the perforated covers, and, part

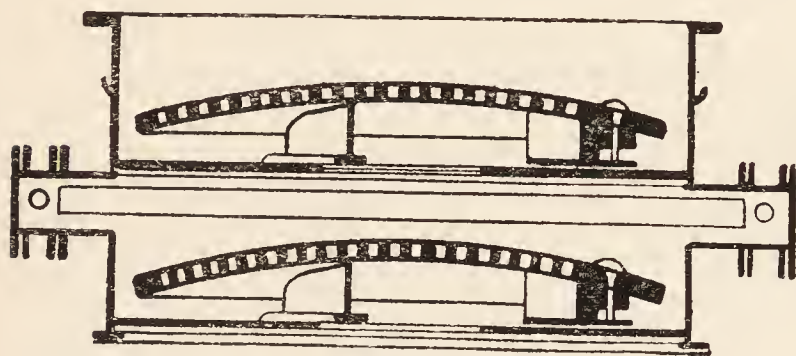


FIG. 17.

passing through the perforation in the mushrooms, and part bubbling round the edges of the mushrooms, come in a comparatively fine state of division in contact with the liquid in the tower. With the assistance of the constant agitation the stream of ammoniated brine carries down with it practically all the sodium bicarbonate precipitated from it.

The increased partial pressure of carbon dioxide in the gases at the bottom of the tower, due to the pressure, increases the speed of the reaction.

One of the most important points in the working of the Solvay towers is (as mentioned in the introduction) the regulation of temperature. The absorption of carbon dioxide by aqueous ammonia produces considerable quantities of heat, the larger part of which is produced in the formation of the ammonium mono-carbonate $(\text{NH}_4)_2\text{CO}_3$. To get rid of this heat, in some cases a supplementary Solvay tower has been added in which the greater part of the mono-carbonate is produced. In other cases part or the whole of the ammonia (NH_3) is mono-carbonated in an intermediate vessel of the type of a tower washer placed between the ammonia vats and the feed pump to the Solvay towers, and which is supplied independently with carbon dioxide from the lime kiln.

It was early found that the output from a Solvay tower was increased by cooling the tower by spraying the exterior with water. For such large diameter towers this external cooling is not convenient nor is it very effective.

Cogswell (Eng. Pat. 1973 of 1887) applied a system of internal cooling pipes, Fig. 17 in sectional elevation and Fig. 18 in diagrammatic

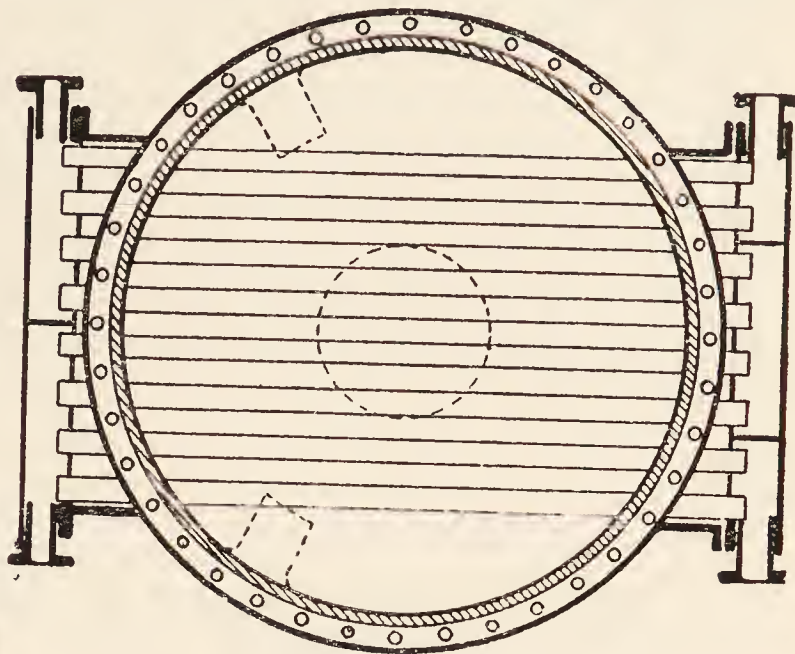


FIG. 18.

plan. The tube plates into which the ends of the tubes are made fast are shown in Fig. 18, but they are omitted from Fig. 17. The water enters Fig. 18 by the right top corner inlet, and the baffle compels it to pass through the two top tubes to the left, where the baffle compels the water to pass through the next two tubes to the right; here the second baffle deflects the water again to the left by the next two tubes, and the last two tubes carries the water to the right and it leaves the cooler by the right-hand bottom corner outlet. As the supply of cold water to each set of eight pipes can be separately regulated, the temperature of every part of the tower can be efficiently controlled.

The top of the tower should be kept as cool as possible to avoid volatilisation of ammonia, and the middle and lower parts should be maintained at a temperature of about 20° , as steadily as possible.

The Solvay tower normally runs two to three months without blocking up; when this occurs all liquor is run out while maintaining the usual agitation caused by pumping in kiln gas. Water is then run into the tower, and the whole boiled up with steam. This dissolves out the soda crusts that have been formed.

Other forms of carbonators.—Numerous other forms of carbonators have been suggested, and some are worked on the large scale. *Vertical type.*—Schreib, D. R. P. 70169; Honigmann, D. R. P. 13782; Schreib, Chem. Zeit. 1890, 492. *Horizontal type.*—One of the oldest apparatus is that of Gossage (Eng. Pat. 422, 1854; Young, Eng. Pat. 2558, 1871). The Boulouvard apparatus, which has been employed successfully in France, is described in Fr. Pat. 125625, 1878; Péchiney, Eng. Pats. 2098 and 5394, 1880, describes a modification of the Boulouvard apparatus.

Stage 4. Filtering the precipitated bicarbonate from the Solvay tower liquor.—Fig. 19 represents a common form of filter. The shell A is of steel plates, and it may be up to 12 ft. diameter. The filter bed B usually consists of a perforated cast-iron plate on which rests a coarse flannel filter cloth, over which is a wire mesh grid to protect the flannel from the spade used to

empty the bicarbonate from the filter. A series of five such filters are connected to a battery of four Solvay towers, and are alternately filled with the liquor and salts flowing from it.

While filling, the space below the filter bed is placed under vacuum, and receives the filtered liquor. When the bed of bicarbonate on the filter has become about 24–28 ins. thick, the stream of liquor is turned on to another filter. As soon as the mother-liquor has been drawn through the salts, the surface of the salt is smoothed over and any cracks, especially round the edges of the vessel, made good. The salts are then washed with water, delivered by a

spray, until the chloride in the bicarbonate has been reduced to the desired extent. When this is done the spray of wash water is stopped, and the vacuum maintained until the bicarbonate is drained as dry as possible. The usual rough test for a normal good grain bicarbonate is that a ball of the salts when pressed in the hand does not yield water.

There is a material loss of bicarbonate in the washing operation, and it is practically impossible to wash the precipitated bicarbonate free from ammonia or sodium chloride without an altogether extravagant loss of bicarbonate, either by solution or by decomposition, losing

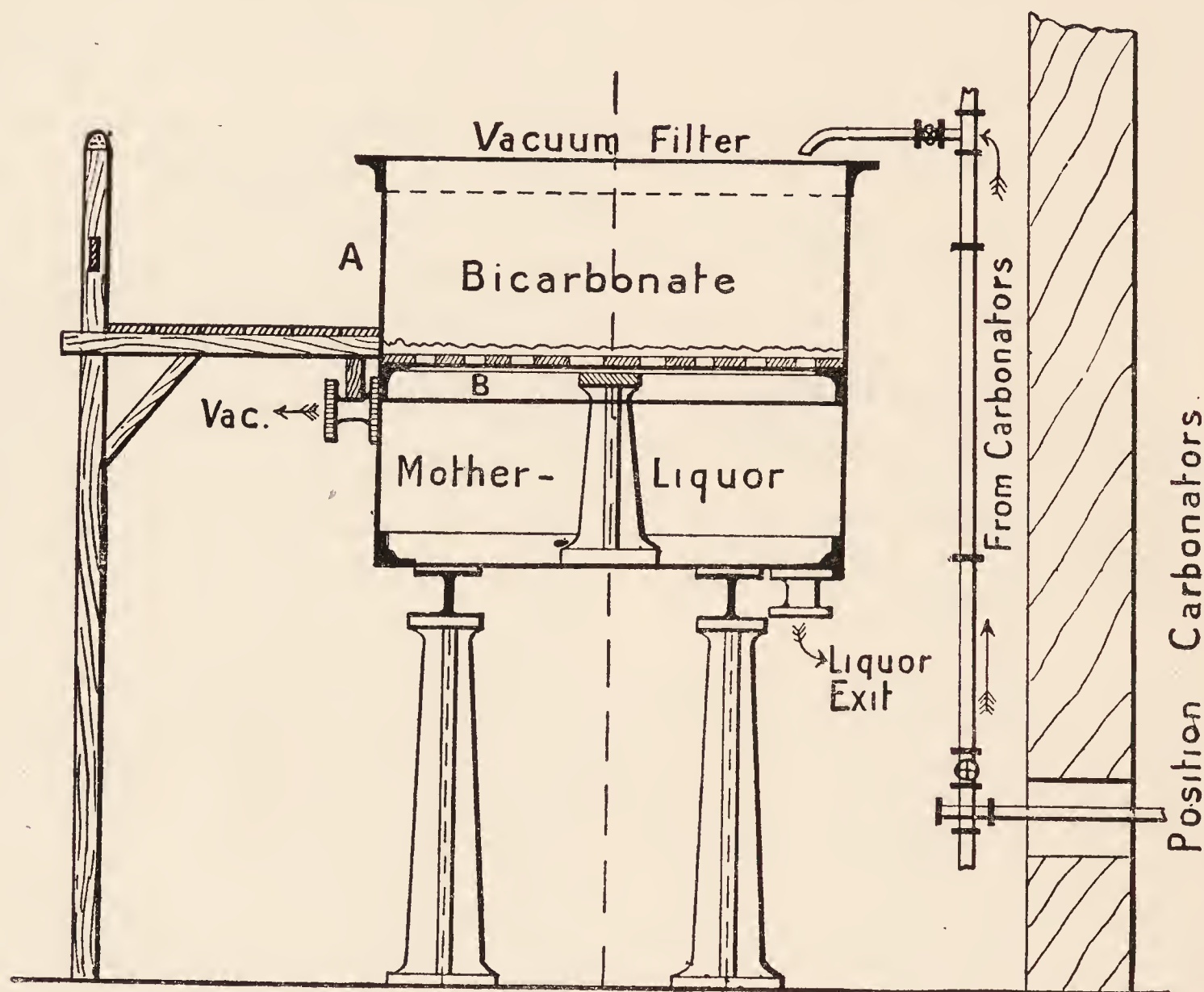


FIG. 19.

carbon dioxide and forming sodium sesquicarbonate. Bradburn gives for these impurities

NH_3	0.56	p.c.
NaCl	0.2–0.7	"
Na_2CO_3	3.0–5.0	"

The efficiency of the washing operation depends more upon the physical condition of the bicarbonate itself than upon apparatus. The physical condition depends on the temperature conditions of the Solvay tower. At low temperatures not only is the precipitate in a very fine state of division, and practically impossible to wash, but it contains ammonium chloride in the solid state, which experience has shown is with the utmost difficulty taken up by the wash water.

After the removal of the vacuum under the filter the mother liquor and wash-liquor are run off into the store tanks or wells, from which

they are afterwards pumped to the ammonia stills.

Several mechanical filters have been devised which permit of continuous and automatic filtering, washing, drying, and removal from the filter bed, thus effecting a material saving in labour.

Figs. 20 and 21 represent the filter patented by Solvay (4725, 1896), in which A is a drum revolving in the vessel B into which the liquor and salts from the towers are fed, and in which they are kept agitated. The drum A slowly revolves about a horizontal hollow axle C connected with a vacuum pump. The periphery of the drum A is formed of a perforated metal sheet, covered with a fine metallic cloth in which a piece of flannel is secured. As the drum revolves the internal suction draws in liquor and forms a coating of bicarbonate on the surface. The cake of bicarbonate as it

travels out of the pulp and round is sprayed with water and is effectively washed, the vacuum dries the thin cake of bicarbonate, after which it is continuously removed by a scraper.

Another mechanical filter is described in Eng. Pats. 7957 and 28791, 1903, taken out by Houghton and the United Alkali Co., Ltd. This filter consists of an inclined rotating dish provided with a false bottom of filtering material. The dish is divided into compartments below the filter bed, which are alternately in communication with the suction device to carry away filtrate, and with a supply of mother-liquor or water to wash the solid matter from the pores of the filtering material. A stream of liquor and salts from the tower is run on to the rotating filter bed, the liquor passes through, drawn by the suction, and the bicarbonate is left as a comparatively thin layer, which in the course of revolution of the dish is washed by a water spray and then automatically removed by a scraper or plough.

From the ordinary filters of the type shown

in Fig. 19 the bicarbonate is discharged by hand into barrows or trollies, in which it is conveyed to the roasters. From the mechanical filters the bicarbonate, as it is continuously removed by the plough, is continuously carried away by a conveyor.

The use of the washed bicarbonate for the manufacture of sodium carbonate anhydrous is described under sodium carbonate anhydrous (see p. 176, method 12), and the use of the washed bicarbonate for the manufacture of commercial bicarbonate is described, after that the recovery of the ammonia from the mother-liquors has been described, for without this recovery the bicarbonate could not be made commercially.

Stage 5. The recovery of the ammonia as ammonia gas.—The ammonia used in the process, with the exception of the unavoidable losses, is recovered by the distillation of the various ammoniacal liquors collected as described above. The larger part of the ammonia is contained in the liquors from the filters, and is present mainly as ammonium chloride, but

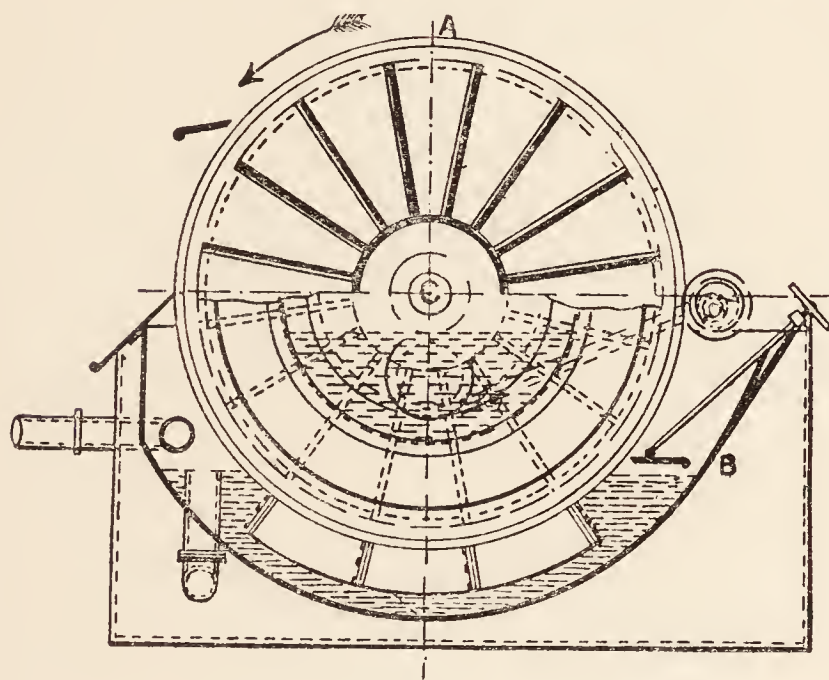


FIG. 20.

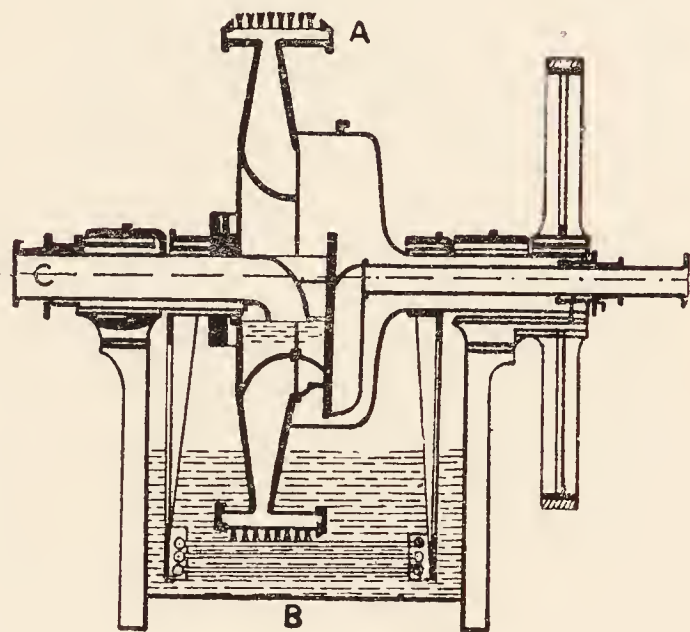


FIG. 21.

15-20 p.c. is present as bicarbonate, and is therefore volatile.

The ammonia losses are made good by the addition of fresh ammonia liquor (from gas works and recovery coke ovens), which contains chiefly ammonium hydroxide, but also some carbonate and sulphide. It is added to the general stock of filter liquor, and both are fed together into the still.

Fig. 22 shows the form of still in general use. A, A is an outer case made of steel plates or cast-iron rings, separated into compartments by cast-iron plates, each with a large-sized hole in the centre, and each hole covered by a mushroom. B is the chamber into which the milk of lime necessary to decompose the non-volatile ammonium salts is run. C, C are a number of compartments, each consisting of a cast-iron ring with a bottom having a central hole covered with a plate.

The filter liquors are fed in at the top of the still through the pipe E, and steam is fed into the bottom of the still by the pipe F (on the further side of the still). As the liquors pass down the upper part of the still or 'heater' they are heated by the steam rising from the

lower half, and the ammonium carbonate and bicarbonate are decomposed and driven off.

The hot liquor containing all its ammonia in the form of non-volatile ammonium salts then passes by the external side pipe into the bottom part of the chamber B, where it is mixed with the milk of lime pumped in through a pipe not shown in the figure. The lime decomposes the ammonium salts, and as the turbid mixture passes down through the compartments A, A, the liberated ammonia is more and more completely driven off by the steam, and the turbid liquid now consisting of a solution of calcium chloride, and sodium chloride with the excess of calcium hydrate, &c., in suspension passes away through the pipe G.

From the top of the still ammonia, steam, and carbon dioxide pass away through the outlet D, at a temperature of 80°-85°.

As has been stated (p. 187, col. 2, par. 2), it has been found that the gases should be cooled so that they enter the absorbers at about 70°. The distiller-cooler, or condenser, may be of various forms, but is usually a vessel built up of cast-iron rings. Near the top of the vessel, and also near the bottom, is a cast-iron tube

plate, into which are expanded a number of tubes. Cooling water is passed through these tubes, entering below the bottom tube plate and flowing away from the top of the top tube plate. By regulating the cooling water supply, the temperature of ammoniacal gases which pass through the central portion of the cooler,

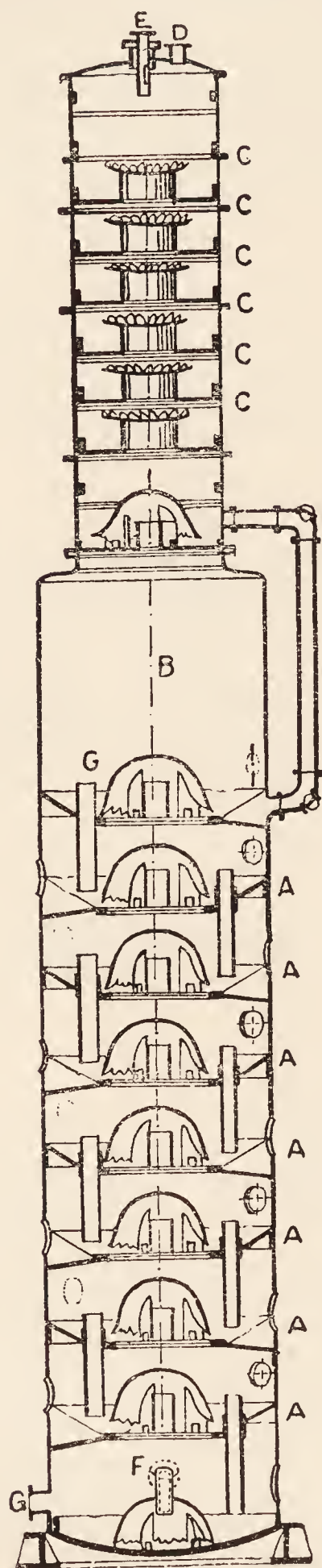


FIG. 22.

and over the exterior of the cold tubes, is reduced to any desired degree. The ammoniacal liquor condensed in the cooler is either run back into the filter liquor store or into the still itself at some point in the upper or heater part.

For the efficient working of the still itself, and for the smooth interworking of the still and the absorber, regularity is required—

1. In the test of the ammonia in the filter liquor feed. It is therefore a matter of importance to watch carefully the average strength of the liquors collected in the filter liquor store tanks.

2. In the supply of the milk of lime, which should always be in slight excess, otherwise there is a loss of ammonia.

3. In the supply of steam, because if there is a deficiency of steam there is incomplete distillation of the ammonia, and it is lost in the exit liquors. If, on the other hand, there is an excess of steam, the cooler will be overworked, and the gases entering the absorber will contain an excess of water, and thus dilute the brine.

The lower parts of the stills gradually become blocked up with scale which adheres to all parts of each compartment, sometimes to the thickness of three inches. From time to time this has to be cleaned away, and the only method available is, after well steaming out the still and allowing it to cool, to chip off the scale by hand. The scaling requires to be done every one to two months, depending on the speed of work.

The waste liquor leaving the still is a solution of calcium chloride and sodium chloride, containing the excess of lime mentioned above, and also fine calcium carbonate, due to the unburnt calcium carbonate in the lime which gets past the gauze strainers of the lime slaker, and also due to any carbon dioxide not driven off in the upper part of the still. The liquor also carries away any other impurities which may have been in the limestone. It is the usual custom to run this liquor through settling ponds, where the solids separate out, after which the solution of chlorides is run away.

It will be noted that the calcium chloride thus run away contains all the chlorine that was originally combined with the sodium which has been converted into sodium carbonate, and, in addition, the liquor carries away unused about 20–40 p.c. of the total salt brought into the process. A very great amount of work has been done to try and utilise the chlorine thus lost by the ammonia soda process, but without success, until recently when it has been used for working up crude zinc oxide or carbonate, a solution of zinc chloride results which by electrolysis yields pure zinc and chlorine gas.

Stage 6. Purification of washed bicarbonate.—The washed bicarbonate could not be used for preparation of baking powders, &c., because it contained too much ammonia salts. It is purified by the three following methods.

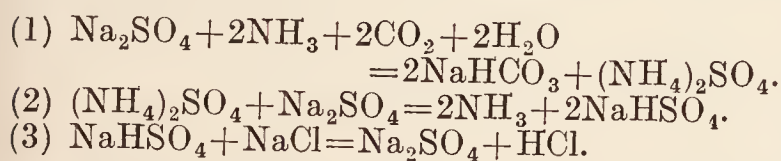
Mond and Jarmay (Eng. Pat. 2996, 1884) dissolve the crude salt at 65°, filter off the insoluble impurities and allow the solution to cool. The bicarbonate separates out in granular crystals, which are drained, dried and ground. The solution can be made at a higher temperature in an atmosphere of carbon dioxide under pressure, but it must be cooled down to 65° before removing the pressure. The mother liquors can be used many times over until they get too rich in ammonia.

Jarmay (Eng. Pat. 23890, 1893) describes improvements made in this process, and states the crude bicarbonate is dissolved in a closed vessel provided with an agitator in which the temperature is maintained by a closed steam coil between 85° to 90°. The escaping vapours

containing NH_3 , some CO_2 and steam, are passed through a multitubular cooler, where they are surrounded by mother-liquor from a former operation. The solution in the dissolver containing bicarbonate and some sesquicarbonate is passed through a filter press and then pumped into an iron tower containing many compartments and water-cooled. Here the temperature of the solution is reduced to 72° . Lime kiln gas is pumped into the bottom of the tower and causes constant agitation. The carbonated liquor and precipitated bicarbonate run from the bottom of the tower on to a filter and the mother-liquor flows back to the dissolver through the cooler mentioned above. Jarmay (Eng. Pat. 3889, 1893) describes the drying of the moist bicarbonate obtained as above in a long covered trough through which the bicarbonate is carried on a conveyor and through which also air, preferably mixed with carbon dioxide and heated to 95° , is blown.

Brock and Hawliczek (Eng. Pat. 8314, 1896) treat the ammonia soda roasted ash or the crude bicarbonate, after removal of the ammonia and part of the carbon dioxide, with steam and carbon dioxide, either consecutively or simultaneously, in order to obtain a pure bicarbonate.

Application of the principle of the ammonia soda process to sodium sulphate.—As the ammonia soda process starting from sodium chloride does not economically yield hydrochloric acid, attempts have been made to work the process using sodium sulphate as the starting-point; in this case the hydrochloric acid is evolved in the production of the sodium sulphate. The process is first mentioned by Bower (Eng. Pat. 8413, 1840), and was afterwards considered by Gerlach and by Weldon (*see* Eng. Pat. 5605, 1883). Gaskell and Hurter were, however, the first to seriously attack the difficulties of the process (*see* Eng. Pats. 5712, 1883; 8804, 1884; and 9208, 1886). The great difficulty was how to deal with the ammonium sulphate formed in the reaction. Gaskell and Hurter's scheme was to heat the ammonium sulphate with sodium sulphate in a current of steam, when the ammonia is liberated and acid sodium sulphate left behind. The process then followed the three reactions—



The second stage of the process was, however, always the stumbling-block, and, owing largely to its cost, this interesting process was not persevered with.

Application of the principle of the ammonia soda process to sodium nitrate.—This was suggested in 1876 by Gerlach and patented in 1877 by Lesage & Co., and again by Chance (Eng. Pat. 5919, 1885). Colson (J. Soc. Chem. Ind. 1910, 190), again, recommends this process as being theoretically more favourable than the sodium chloride process.

Properties of sodium bicarbonate NaHCO_3 .—A fine white crystalline powder of sp.gr. 2.206. 100 parts water dissolve

at	0°	10°	20°	30°	40°	50°	60°
NaHCO_3	6.90	8.15	9.60	11.10	12.70	14.45	16.40

The solubilities at 0° to 60° in presence of

(a) NaCl , (b) Na_2CO_3 , and (c) NaCl and Na_2CO_3 , are given numerically and diagrammatically in Phil. Trans. Roy. Soc. A. 223, pp. 35–87, by Freeth.

Exposed to the air sodium bicarbonate loses a little carbon dioxide until it contains sufficient Na_2CO_3 to arrest further decomposition; this Na_2CO_3 may be easily washed out, but only to be replaced by more Na_2CO_3 .

The composition of commercial refined bicarbonate is given as—

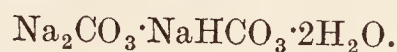
NaHCO_3	97.2
Na_2CO_3	1.9
NaCl	0.35
H_2O	0.82

(*See* Lunge's Alkali, vol. iii. p. 211.)

On gentle heating it decomposes first into sodium sesquicarbonate, which *see* below, and then into the normal carbonate (*see* p. 176, method 12).

Applications.—Sodium bicarbonate is chiefly used, as already mentioned (p. 182, col. 1, par. 3), as the first step in the preparation of anhydrous sodium carbonate (*see* p. 176, method 12), but it enters commerce for the following purposes: as a chief ingredient of baking powder (*see* vol. i. p. 501); as the carrier in the washing blue used in laundries; as the source of carbonic acid in the manufacture of mineral waters, for which it has the advantage over CaCO_3 —which was formerly used for the purpose—of yielding double the quantity of CO_2 gas per unit of sulphuric acid and of leaving a soluble salt in the generator, viz. Na_2SO_4 instead of CaSO_4 ; for effervescing drinks; dry soaps; soap powders; medicinal purposes; and for washing delicate fabrics. For the use of phenolphthalein for detection of sodium carbonate and chloride in sodium hydrogen carbonate, *see* Richter (Chem. Soc. Abstr. 1913, ii. 152).

Sodium sesquicarbonate



This salt is found in many mineral waters (especially those of Aix-la-Chapelle, Karlsbad, and Vichy), in the 'natron lakes' of Hungary, Egypt, Central Africa, the Caucasian steppes, and in those of North and South America; also as efflorescences in such steppes, especially in the neighbourhood of natron lakes. These efflorescences or crusts are formed either by the partial or entire drying up in summer of such lakes or ponds, or else by the evaporation on the surface of the soil of subsoil moisture containing this salt, a continuous supply of subsoil moisture being always brought to the surface by capillary action. The soda thus obtained in various places is known by the names *natron*, *trona*, or *urao*. 'Urao,' according to Chatard (Bulletin No. 60, U.S. Geological Survey, 1887–1888), is essentially a carbonate of the formula $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$, and is the most usual form of 'natural soda.'

The oldest-known occurrence of natural soda is that in Lower Egypt, where the natron lakes dry up in summer, leaving crusts of salt behind; in other places the 'trona' appears as efflorescences on the ground, consisting essentially of sodium sesquicarbonate. Several thousands of tons of this article are yearly exported from Alexandria, principally for soap-making. Similar

alkaline waters, earths, and salts are widely known in India and Tibet. Enormous quantities of soda are found in the lakes and steppes of the 'Alkali Plain' and other parts of the great desert east and west of the Rocky Mountains. One of the most considerable of these occurrences is in Owen's Lake, in California, which, according to Chatard, contains per litre :

Na_2CO_3	.	.	.	26.96	grms
NaHCO_3	.	.	.	5.71	"
Na_2SO_4	.	.	.	11.08	"
NaCl	.	.	.	29.41	"
KCl	.	.	.	3.14	"

with a little silica, alumina, calcium, magnesium, and boric acid. This lake contains from twenty to forty millions of tons of sodium carbonate, which is easily obtained in an almost pure state by solar evaporation in shallow ponds. Another similar lake is Searles Lake. See Chem. and Met. Eng. from 1914 onwards.

The Magadi Lake in British East Africa (Kenya Colony) in area is about 30 square miles in extent; it is estimated to contain some 200,000,000 tons of soda. The following analysis is by A. Gordon Salamon :—

$\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$.	.	92.85
NaHCO_3	.	.	5.90
NaCl	.	.	0.36
SiO_2	.	.	0.07
$\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$.	.	0.04
Water (by diff.)	.	.	0.78
			100.00

Magadi, which in the native dialect denotes 'soda,' is situated about 370 miles from the port of Kilindini, and some 60 miles to the south of Nairobi. The Magadi Lake occurs at about 2000 ft. above the level of the sea, and lies in a deep depression called the Rift Valley, at some 3000 ft. below the level of the Central African plateau that surrounds it.

The development of the waters of this natural soda lake was undertaken by the Magadi Soda Company, Ltd., formed in 1911 with a capital of £1,321,500. This company went into liquidation in 1923, and in 1924 a new company was formed in accordance with a re-organisation scheme put forward by Brünner, Mond & Co., Ltd. Under this scheme Brünner, Mond & Co., Ltd., have put up a new capital, and have taken the whole of the ordinary shareholding, and the majority of the directors of the new concern are members of the board of Brünner, Mond & Co., Ltd.

A branch line of about 92 miles is being constructed from the Uganda railway to Magadi, and a deep-water pier and sidings are in the course of construction at Kilindini, thereby it is anticipated that the development of the waters of the Magadi Lake will result in a considerable extension of the trade in soda compounds to the Far East, including India, China, Japan, South Africa, Cape Colony, Australia etc. Kilindini is well situated for supplying these important markets. The anticipation of this realisation was delayed by the Great War of 1914.

It is not impossible that these ancient soda deposits, when worked by modern methods, may in a few years again become as of old times

the main source of the world's supply of soda. For the conversion of natural soda into soda ash Na_2CO_3 , see p. 158, col. 2, method 1.

The sesquicarbonate is made artificially by Watts and Richards (Eng. Pat. 13001, 1886) by preparing a solution containing soda ash and bicarbonate in the above proportions and allowing it to crystallise not below 35° , keeping it agitated all the time. Such a solution can also be prepared by heating solid sodium bicarbonate so as to deprive it of about one-third of its carbonic acid and then dissolving the residue.

The composition of commercial sesquicarbonate is:

$\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$.	.	99.28
NaHCO_3	.	.	0.10
Water	.	.	0.43
NaCl	.	.	0.18
Insol.	.	.	0.02
			100.01

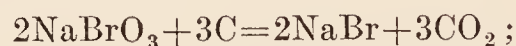
(See Lunge's Alkali, vol. iii. 212.)

The sesquicarbonate crystallises in fine needles, does not effloresce or deliquesce, and is readily soluble in water. Its principal employment is for wool washing, linen and other washing. It is also used with advantage in dressing ores by flotation (Met. & Chem. Eng. 17, 543).

Sodium bromide NaBr can be prepared by neutralising a solution of sodium hydroxide or carbonate with hydrobromic acid, but is usually made technically by adding bromine to a hot solution of caustic soda, mixed with powdered charcoal. Sodium bromide and bromate are first produced:



on evaporating the solution to dryness and heating the residue, the bromate is reduced by the charcoal



the fused mass is dissolved in water, filtered, and crystallised above 50° .

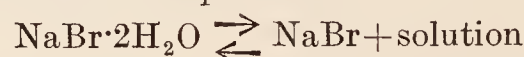
The crystals are anhydrous NaBr , and their form belongs to the regular system; the sp.gr. is 3.014; the m.p. 765° ; the sp.gr. of the salt being $2.2125-0.0080(t^\circ - 900^\circ)$. The substance dissolves in water with considerable absorption of heat; the solubility is (De Coppet, Ann. Chim. 1883, [vi.] 30, 420):

Temp.	-10°	0°	20°	40°	60°	80°	100°	120°
Grams								
NaBr in								
100 grms.								
water	75.1	79.5	90.3	105.8	117	118.5	120.5	122.5

the saturated solution boils at 121° . It is soluble at the ordinary temperature in 14 parts of ethyl alcohol or 4.6 parts of methyl alcohol. It also is soluble in acetone.

Sodium bromide is occasionally employed in medicine in place of the potassium salt, which it resembles in its physiological effects.

When solutions are made to crystallise at ordinary atmospheric temperatures, the hydrate $\text{NaBr} + 2\text{H}_2\text{O}$ is obtained in monoclinic crystals. The conversion temperature



is 50.7° . The sp.gr. of $\text{NaBr} \cdot 2\text{H}_2\text{O}$ is 2.176.

When solutions are crystallised at extreme winter temperature, the hydrate $\text{NaBr} + 5\text{H}_2\text{O}$

has been obtained in needles which melt at -23.5° .

The sp.gr. of the solutions at $19.5^{\circ}/4^{\circ}$ (vacuum) are—

5 p.c.	10 p.c.	15 p.c.	20 p.c.	25 p.c.
1.038	1.078	1.123	1.172	1.223
30 p.c.	35 p.c.	40 p.c.	45 p.c.	50 p.c.
1.278	1.341	1.407	1.480	1.561

For the sp.gr. of sodium bromide solutions, see Kremers (Pogg. Ann. 1855, 96, 39); for their electrical conductivity, see Ostwald (Allgem. Ch., Leipzig, 1893), and for their refractive indices, see Boriesius (Wied. Annalen, 1895, 54, 233).

The double salt $2\text{NaBr}\cdot\text{NaBrO}_3$, 'Bromine Salt,' see vol. i. p. 694. For the commercial estimation of bromides in sodium chloride, see Chelle (Chem. Soc. Abstr. 1915, ii. 174).

Sodium chlorate NaClO_3 . For the preparation of sodium chlorate see vol. 2, p. 213, col. 1, to p. 214. The melting-point of sodium chlorate, according to Retgers, is 248° . According to Poppe the solubility in water at 30° is 51.52 p.c. of chlorate. The following numbers are given by H. C. Bell (J. Chem. Soc. 1923, 123, 124, 2713-2714):—

Tempe- rature	0°	10°	20°	25°	30°	35°	40°	100°
NaClO_3 p.c. of solu- tion	44.32	46.70	48.95	50.13	51.30	52.38	53.54	67.10

For the crystal structure of sodium chlorate, see Wilhelm Kiby (Zeitsch. Physik, 1923, 37, 213). According to J. Beckenkamp (Zeitsch. Physik. Chem. 1923, 20, 414), the crystal structure suggested by Kiby (Absts. Chem. Papers, 1923, ii. 687) for sodium chlorate requires modification in order that the optical activity of this substance may be accounted for. According to the amended structure, the two oxygen atoms in the formula $\text{NaOCl}\leq\text{O}$, which are connected by double bonds with the chlorine atom, are separated in the crystal from the chlorine atom by a distance which differs from the distance between the chlorine atom and the third oxygen atom. This difference, which is responsible for the optical activity of sodium chlorate, cannot be detected by X-ray measurements (Chem. Soc. Abstr. 1924, 126, ii. 143).

For the structure of crystals of sodium bromate and sodium chlorate, see L. Végard (Zeitsch. Physik. Chem. 1923, 18, 379); A. Karssen (Rec. trav. chim. 1923, 42, 904); Kolkmeier, Bijovet and Krassen (Zeitsch. Physik. Chem. 1923, 20, 82). For the crystal structure of sodium chlorate, see Kolkmeier, Bijovet and Krassen (Chem. Soc. Abstr. 1921, ii. 200).

Sodium chloride. *Chlorure de sodium, hydrochlorate de soude, sel marin*, Fr.; *Steinsalz, Kochsalz, Salz, Salzsaures Natrium, Chlornatrium*, Ger.; *sal*, Lat.; $\alpha\lambda\varsigma$, Greek.

Sodium chloride, or common salt, is found in nature as the mineral *halite*, or *rock salt*. It crystallises in cubes, occasionally associated with other forms derived from the regular system. From solutions containing carbamide or formamide it crystallises in octahedra (cf. Ritzel, Zeitsch. Kryst. Min. 1911, 49, 152, who has shown how the crystal habits of sodium chloride varies with the solvent, the different crystal faces being attacked or formed at

varying rates depending on the nature of the solvent). For the growth and dissolution of crystals of sodium chloride in solutions containing carbamide, see Schnorr (Zeitsch. Kryst. Min. 1915, 54, 289; Chem. Soc. Abstr. 1917, ii. 469). For the solubility of the cubic and octahedral faces of sodium chloride, see Le Blanc and U. E. Lissafov (Chem. Zentr. 1914, i. 609; Chem. Soc. Abstr. 1914, ii. 268). For the growth and dissolution of crystals of sodium chloride, see Poppe (Jahrb. Min. 1914, Beil. Bd. 38, 363; Chem. Soc. Abstr. 1921, ii. 90). For the limits of formation of mixed crystals between potassium chloride and sodium chloride, see Nacken (Sitzungsber. K. Akad. Wiss. Berlin, 1918, 192, from Chem. Zentr. 1919, i. 77; Chem. Soc. Abstr. 1919, ii. 281). See also Tammann (Nachr. Ges. Wiss. Göttingen, 1919, 422, from Chem. Zentr. 1920, i. 604; Chem. Soc. Abstr. 1920, ii. 373). Hardness, 2; sp.gr. 2.2. Sodium chloride is colourless and transparent when pure, but in the form of rock salt it is usually tinged yellow, red, brown, or green. It melts at 803.4° (Ferguson, Roy. Soc. Canada, 1921, 15, 50). According to H. S. Roberts (Physikal. Rev. 1924, 23, 386; Chem. Soc. Abstr. 1924, 126, ii. 300), the melting-point is 800.4° , it is slightly volatile at high temperatures, especially in a current of moist air due to the hydrolysis of the salt by the water.

In 1809 Gay-Lussac and Thenard (Arcueil Mem. Phys. 1809, 2, 339) reported that silica and sodium chloride react in the presence of water vapour to give hydrochloric acid and sodium silicate. They noted that no reaction occurs at a white heat in the complete absence of moisture, although sodium bromide and iodide are decomposed under similar conditions; Schönbein (Pogg. Ann. 1849, 78, 517) confirmed these observations (Clews and Thompson, Chem. Soc. Trans. 1922, 1442). See also English and Turner (Chem. Soc. Journ. 1914, p. 162). For volatility, see Wagenaar (Pharm. Weekblad. 1913, 50, 1214; Chem. Soc. Abstr. 1913, ii. 1073). Thrown upon a coal fire it produces a blue flame surmised to be due to compounds of copper derived from pyrites in the coal, A. Smithells (Nature, 1922, 109, 745; cf. Merton, *ibid.* 1922, 109, 683; Chem. Soc. Abstr. 1922, ii. 645). For the dissociation, see Thompson, (Trans. Ceramic Soc. 1918, 17 (2), 340; Chem. Soc. Abstr. 1918, ii. 441).

Owing to its wide distribution on the earth sodium chloride has been known from the very earliest times. It is frequently mentioned in the Bible. The Jewish law commanded the people to season the meat offering with salt (Lev. ii. 13). The Jews used a very impure argillaceous kind of rock salt, from which they extracted the salt by means of water, leaving the clay as mud. This mud still contained some salt, and was either used directly for agricultural purposes, or was allowed to lie on the manure heaps before being used, where, after prolonged exposure in presence of nitrogenous matter, the salt was partially converted into sodium nitrate. Hence we find the expressions (Matt. v. 13), 'Ye are the salt of the earth: but if the salt have lost his savour, wherewith shall it be salted? it is thenceforth good for nothing, but to be cast out and trodden under foot of men'; and (Luke xiv. 34) 'Salt therefore is good: but

if even the salt have lost his savour, where-with shall it be seasoned? It is fit neither for the land nor for the dunghill: men cast it out.'

Occurrence of salt.—Salt is very widely distributed. Immense deposits of it, in the form of rock salt, are found in many parts of the world. It is the principal solid constituent of sea-water and of many salt lakes, and is found in brine springs and most mineral waters. There are few countries in which it does not occur, as also there are but few geological formations from which it is absent. In America rock salt is met with in very old strata, some of the recent discoveries of it being in the Silurian rocks.

In New York State, Michigan, and in Ontario it is found in the Upper Silurian formation, and usually lies at a depth of over 1000 ft. from the surface. South of Rochester (New York), in what is known as the Warsaw district, the rock salt is found in three superposed beds. The top layer is 60 ft. thick; then follows 10 ft. of shale. The second bed is 20 ft. thick, and is separated from the third by 30 ft. of shale. The Ontario deposits are found in the counties of Essex, Lambton, Middlesex, Huron, and Bruce lying along the shores of lake Huron. The beds are struck at depths varying from 970 to 1650 ft., and in some places they reach a thickness of 250 ft. It has been found at Kwinitza on the Skeena river in British Columbia, 45 miles from Prince Rupert, at 50 to 250 ft. from the surface (*Chem. Trade Journal*, May 17, 1913, 522), and in Nova Scotia.

Rock salt is also known in Manitoba and Athabasca (*see Geology and Economic Minerals of Canada*, Depart. of Mines, Ottawa, 1909).

The rock salt found in Michigan is principally at Saginaw, Detroit, and Bay City. In Utah there are extensive deposits embedded in red clay. Salt is also found in Virginia, Ohio, Louisiana, and Kansas. The deposits which occur in Louisiana lie in the post Tertiary formation, while those of Kansas are found in the Permian. The latter have been proved to be most extensive, reaching into Oklahoma.

Rock salt is known in Mexico, Colombia, Venezuela, and the Argentine. There are immense deposits in Chile and Peru. It is found at Kulpi in Armenia, at Nachitschevan, and in many places in the Caucasus. It is claimed that the rock salt deposit near the town of Iletz Zashtchiti in the province of Orenburg, S.E. Russia, is the richest in the world (*Chemical Trade Journal*, Feb. 1910, 179).

The district of Ferghana Turkestan is rich in salt deposits. Rock salt is widely found throughout the basin of the river Donetz in southern Russia, and at Vsolje where it occurs in Oolitic limestone. It is also known at Balachna on the Volga, at Irkutsk in western Siberia, and in the Crimea.

On both sides of the Carpathians rock salt abounds, most of it in Tertiary formations. In Galicia the principal mines are at Wieliczka (where the deposit is said to be 1200 ft. thick), at Stebnick (where three beds have been found), and at Bochnia. Transylvania and Wallachia possess many mines. In the Tyrolean Alps rock salt occurs in Oolitic limestone. In the Austrian portion, the principal deposits are at Salzburg, Aussee, Ischl, Hallstadt, and Hallein; while in Bavaria, salt is found at Berchtesgaden

and Reichenhall, and in Hungary at Marmores. At Volterra, in Italy, there are several deposits at 150–308 ft. from the surface. There are two salt mines in Czecho-Slovakia; one at Solnohrad near Presov (Slovakia), the other at Marmarozska Solotvina (Rusina). The deposits are apparently very extensive.

In Spain rock salt is plentiful; but the most remarkable deposit is that of Cardona (Barcelona), where there are two hills of very pure white salt, each about a mile in circumference.

Almost inexhaustible supplies of rock salt are to be found in Germany in the district round Stassfurt and in the 'salt-mines province' of Bavaria. The Stassfurt salt contains 98 to 99 p.c. of sodium chloride, whereas rock salt obtained from other German mines is of 90 p.c. purity. The Bavarian salt is obtained by flooding the mines and concentrating the brine thus formed. The works at Schoenebeck in the Magdeburg district have an average annual production of 60,000 tons, and constitutes the largest single enterprise of this kind in the continent of Europe. Other important mines are situated at Egestorf, Lueneburg, Stade, Heilbronn-am-Neckar, and Salzungen. For inland consumption, the salt is sold directly to the trade, but for export it is sold exclusively by the Salz-Ausfuhr Gesellschaft, Berlin. The production in 1921 comprised: rock salt, 1,876,540 metric tons; brine salt, 317,060 tons; panstone and waste, 6920 tons; salt by-products, 81,780 tons; figures which compare with 1,332,180 tons, 678,770 tons, 107,110 tons, and 105,560 tons, respectively, in 1913. The decline in the production of by-products and brine salt is ascribed to the shortage of coal. Since April 1, 1923, the rock salt producers in Germany have been combined to form the Steinsalz-Syndikat G.m.b.H., Berlin, which replaces the former convention (*J. Soc. Chem. Ind.* 1923, 42, 941).

Salt is also found at Heilbronn in Württemberg, Wimpffen in Hesse, and Rappennau in Baden, at Langenberg and Köstritz in Central Germany, at Gera in Reuss, at Buffleben in Coburg Gotha, and at Artern in Prussia.

Rock salt is found in the province of Overijssel, Holland (*Chem. Zeit.* April 18, 1917, 334).

Deposits are found in the Vosges district at Dieuze and Vic in Lorraine, and near to Nancy in France in Keuper marls. Switzerland possesses salt at Bex in the Rhone valley found in the Lias. It also occurs at Rietheim in Aargau at 665 ft. from the surface (*Chem. Zeit.* Feb. 20, 1913, 230).

The Pyrenees are rich in brine springs and rock salt deposits. The beds of Dax and Villefranche are probably Tertiary. At Jebel Usdum, south of the Dead Sea, there is a hill which consists throughout of a single mass of rock salt, covered with a thin layer of calcareous marl. Salt is found in Algeria in cretaceous rocks, and in Abyssinia. In the interior of Libya it is found associated with limestone in cliffs. Herodotus mentions five mountains which lie about equal distances from one another, across a tract of country 10 days' journey in extent (*see H. B. Tristram, The Great Sahara*, 72). It has been found in Somaliland and in S.W. Africa (*Bull. Imp. Inst.* April–June, 1915).

Rock salt is found in India in the red marls and sandstones of the Devonian group. The salt

range of the Punjab contains hills of very pure salt and runs across the districts of Jhelum and Shakpur from the bank of the Jhelum river to Kalabagh in Bannu district. Similar deposits are found in Kohat and Mandi.

In China the salt bed is a triangular tract having the Min river from Ching-ting-fu to its junction with the Yangtze at Sui-fu for its base, and its apex near Tzelintsing an area of some 1500 square miles.

The first discovery of rock salt in the British Isles was made at Marbury near Northwich in Cheshire in the year 1670.

In 1779 it was found at Lawton in Cheshire, and deeper borings at Marston in 1781 revealed the existence of a second or lower bed of salt. These Cheshire beds lie in the Saliferous marls of the Upper Trias formation above the New Red Sandstone, probably identical with the Keuper marls and Bunter sandstone of Germany. At Northwich the top bed is about 75 ft. thick, and lies 135–150 ft. below the surface. It is covered by boulder sands, clays, and red or blue marl. Below the top rock salt there is a bed of hard marl 30 ft. thick, which contains here and there veins of salt and masses of gypsum. Under this a second bed of rock salt is found about 80–90 ft. thick. Deeper borings reveal the presence of successive thin beds of salt. At Marston near Northwich the Salt Union drilled a borehole 2610 ft. deep, starting at 77 ft. above ordnance datum, and found a bed of salt 90 ft. thick at 124 ft., then 28 ft. of marl, succeeded by rock salt 92 ft. thick. Below this they found marl and thin beds of salt for 966 ft., and then passed through sandstone and marl or pure sandstone for 1310 ft.

A borehole over 2000 ft. deep has been drilled at Holford (3 miles east of Marston) that has shown the existence of beds of rock salt down to 1027 ft. from surface, aggregating 503 ft. thick.

At Winsford in Cheshire the beds are similar to those at Northwich, the top rock being about 70 ft. thick and the bottom 120 ft. Rock salt is also found in Cheshire at Sandbach and Lawton. In a paper on the Geography of Central Cheshire, with special reference to the salt industry, Mr. W. J. Lewis states that there were two layers about 90 ft. thick, and it had been shown recently that the salt field extended a good deal further south than was previously thought. Making a very conservative estimate, it was probable, at the present rate of output, that the Cheshire salt field would last another thousand years. The salt trade grew steadily until the early eighties, after which it went down to 57 p.c. of the record output of over two million tons in 1884, and now stood at about 72 p.c. of that record. The decline was due to the development of other salt fields in the British Isles; to the competition of Central Europe, where there were pure deposits of natural rock salt; to the development in America; to the competition of tropical countries where sea salt could be produced; and to some extent, to tariff barriers. In the early 'eighties the Cheshire industry dominated most of the world markets, but since then many of its customers had developed their own resources, and the future of the industry lay with the development of the alkali trades based upon salt (*cf.* J. Soc. Chem. Ind. 1923, 42, 430). At Droitwich and

Stoke Prior in Worcestershire the salt beds lie in the same formation as in Cheshire. At Shirley Brook, in the same county, rock salt is found 273 ft. below the surface. It is met with at the village of Preesal, near Fleetwood in Lancashire, at a depth of 278 ft. (*see* Thompson, Trans. Manchester Geol. & Mining Soc. 30, 105), and is also found near to Barrow-in-Furness and in the Isle of Man at the Point of Ayre at 617 ft. below the surface (*see* Dawkins, Quart. Journ. Geol. Soc. 58, 1902). At Stafford Common in Staffordshire it is 263 ft. deep. Salt was found in 1911 at Dunball near Bridgewater in Somerset (*see* Pro. Geol. Assoc. 1911, vol. xxii. part 5, pub. E. Stamford). In the neighbourhood of Middlesbrough, in the county of Durham, rock salt has been proved to exist over an area of 20 square miles. The most northerly bore-hole is at Greatham, where salt was found at a depth of 889 ft. below sea level. To the south, at North Ormesby, in Yorkshire, the bed is 1340 ft. from the surface, while the most easterly bore-hole at Lackenby strikes the salt at 1685 ft. (119 ft. thick), and the most westerly one at Haverton Hill reaches it at 797 ft. The average thickness of the main bed of salt is 84 ft. It lies in marls below a thick bed of red sandstone (*see* Durham Salt District, by E. Wilson, Quart. Jour. Geol. Soc. Nov. 1888; also John Marley on the Cleveland and South Durham Salt Industry, N. of England Inst. of Mining Engineers, 1892, 27). Rock salt is found at Duncrue and Eden near Carrickfergus, and at Magheramorne near Larne in Ireland.

Origin of rock-salt deposits.—The great variability in the position of the salt deposits renders it impossible to consider them as constituting a definite geological formation, but points to the probability that their origin is due either to volcanic action or to the evaporation of water which held the salt in solution. The great argument in favour of an igneous origin rests upon the fact that sodium chloride and hydrochloric acid are emitted by volcanoes; but the occurrence of layers of bitumen and certain organic remains, together with the fact that cavities containing liquids are found in the rock salt, renders this theory untenable.

The general character of the beds, too, favours the assumption that they are of aqueous origin. They are rarely found filling cavities or dykes after the manner of volcanic rocks, but are in layers of very considerable area. These immense beds of rock salt most probably owe their origin to the evaporation of inland seas, and a careful examination of their constitution affords evidence which goes far to prove this theory. The manner in which the deposits were formed appears to be as follows. When, by slow upheaval of the land or by the accumulation of a bar or sand bank, a portion of the sea became partially shut off, the heat of the sun was sufficient to evaporate as much water as was supplied by the sea or by rivers.

Then the volume of water in the part so separated became gradually richer in dissolved salts. The upper layers when concentrated by the sun became specifically heavier and sank to the bottom, the more dilute rising to take their place. As the quantity of salt in solution rose, all those living organisms which were endowed with the means of locomotion left

their homes and returned to the open sea, while those which were lacking in this particular died off. Their remains (such as did not dissolve) are found as insignificant impurities in the gypsum which formed around them. For by degrees the lower portion of the water became so rich in mineral constituents that it could no longer retain them in solution, and they began to separate out. The least soluble salt was, of course, the first to deposit, and this was followed by the others in the inverse order of their solubility. The calcium carbonate and ferrous carbonate, if present, would precipitate first, and then the calcium sulphate would follow in the form of gypsum. As the degree of concentration still continued to rise the sodium chloride began to separate out, depositing on the bottom of the basin in a hard compact mass. In cases where the connection with the sea was still maintained, or where rivers continued to send in water, these various phases would be to a certain extent contemporaneous; for the incoming water would bring with it fresh quantities of calcium carbonate and calcium sulphate, and these salts would precipitate along with the sodium chloride. Nor would this separation of the salts in the inverse ratio of their solubilities proceed with absolute exactitude, for the less soluble might carry down with them minute quantities of the more soluble ones. For instance, it is by no means uncommon to find magnesium sulphate mixed with rock salt, especially where there has been aluminous mud washed in to serve to carry it down. Again, certain combinations of the same salt occur, such as *simonyite*, and *bischofite* is found in solution in cavities in rock salt in Cheshire, where also *hydrophilite* is not infrequently found. As the sodium chloride continued to deposit, the mother-liquor gradually grew richer in the more soluble salts until the point was reached when they too began to crystallise. Potassium chloride and magnesium chloride separated from the solution in combination as the mineral *carnallite*. Potassium sulphate, magnesium sulphate, and magnesium chloride became associated as *kainite*, while some of the magnesium sulphate crystallised in the form of *kieserite*.

It is obvious that when the supply of fresh water from the ocean was continued at all there would be a deposit of salt accompanying the more soluble substances. The calcium sulphate, however, which precipitated from this sea-water would, in falling, pass through the layers of mother-liquor which had reached a high degree of concentration; hence it crystallised as *anhydrite*. The whole of this process of crystallisation was, of course, subject to an immense variety of disturbing influences. The rate of deposition would vary greatly with the season of the year, not only on account of the heat of the sun and the height of the tides, but also on account of the amount of water due to the rainfall. There were probably actual changes in climatic conditions giving at one time a tropical heat and rapid deposition of salt, and at another copious rainfall which arrested crystallisation and caused the rivers to bring down plentiful supplies of mud. In examining beds of rock salt we find evidences of such disturbances in the frequent occurrence of layers of clay, sandstone, or marl, which show that

during certain periods there was little or no deposit of salt. In many cases the disturbance was sufficient to remove the whole of the mother-liquors, and there we find little or no trace of the potassium and magnesium salts.

Such is the generally accepted theory of the formation of the great deposits of rock salt. The ocean has for ages been receiving the waters of rivers and springs charged with matter dissolved during the passage of the water through or over the various rock formations. Such substances as were required to build up the structure of marine animals and plants were by them extracted from the water; the rest would obviously, in course of time, accumulate, because the volume of sea-water was kept nearly constant by continual evaporation.

Such formation of salt deposits may be seen proceeding at the present time, two of the best examples are afforded by the Kara Boghaz or Black Gulf on the eastern shore of the Caspian Sea and the Runn of Cutch in India (*see* Thos. Ward, *Trans. Manchester Geo. Soc.* 18, 396; *Riemann, Monographien über Chemischtechnische Fabrikations-Methoden* Band, xviii.; Halle, 1909, 8).

Rock salt. Rock salt is always found in England associated with a coloured marl, and through having undulating lines of this impurity running through its mass, it generally presents the appearance of stratification.

The tinge of colour varies with the colour of the marl and marlstone with which it is interstratified. It varies from dark red or brown to light amber or white. The yellow rock salt is preferred, on account of its greater purity. The following table shows the composition of the salt obtained from deposits in various parts of the world.

The Cheshire salt mines which are now being worked are all in the lower bed. The rock obtained is purer than that from the upper one, and there is less trouble required to keep out surface water and brine. The modern mine is provided with two shafts placed from 10 to 15 yards apart, with generally (unless the winding shaft be tubed) another permanent shaft for pumping the surface water, sunk only as deep as the water penetrates. In sinking the shaft it is especially requisite to protect the rock salt at the sides from being dissolved by water. All such shafts are roofed over to keep out rain and snow, and are carefully cased down to a solid foundation below where surface water penetrates in the ground. The casing was originally made of wood; but lately this has been replaced by iron. The method of procedure in Cheshire is as follows:—

A solid foundation, such as is generally to be found at a certain bed of marlstone between the top and bottom beds of rock salt, is obtained, and then a ledge 12 ins. wide all round is cut in it, care being taken to remove any small concretions of rock salt which may be in the marl. A bed of concrete is cast upon this ledge and carefully dressed on the surface to receive a cast-iron ring. The bottom length of tubing (called the bell mouth) is generally about 6 ft. long, and is in three segments which, when united, taper from a diameter of about 4 or 5 ft. at the bottom to 3½ ft. at the top, and on this begin the iron cylinders or tubes 3½ ft. diameter and 6 ft. long. The space behind the bell

mouth is carefully filled with cement rammed well down to the concrete foundation.

In the bottom bed workings the height of the rock salt that is being worked varies from 15 to 18 ft. in Cheshire, and from 30 to 40 ft. at Carrickfergus. The mode of working the mines in both districts is to drive out in the upper part about 5 ft. 9 ins. high, which is called the 'roofing,' and to follow up with what is called the 'benching,' leaving pillars of rock salt to support the roof. In driving the roofing a little holing and cutting has to be done with a pick, and as much as possible is blown out with gunpowder, after which the roof is dressed off with a pick. The benching in Cheshire varies from 9 ft. 3 ins. to 12 ft. 3 ins. in thickness, and in Ireland from 24 ft. 3 ins. to 34 ft. 3 ins. This is blown off by a succession of shots, arranged in a slanting direction from the top to the bottom. In some of the mines machines are used. In charging the shot the fine rock salt made in drilling the hole is put next to the powder and coarse-grained rock salt upon that. The stemmers and prickers are all made of iron, as rock salt does not strike a light with iron or steel.

Flat hemp ropes are generally used for winding. In some cases iron-wire rope is used, but it has to be kept well greased to prevent it rusting. Tram roads are used below ground. It is found by experience that the pillars which are left to support the roof should be in proportion to the depth of the mine. At a depth of 330 ft. it is found necessary to leave 1 pillar for every 11¼ times its area of rock worked. The pillars are left 10 yards square, and stand 25 yards apart. There is a crushing and a grinding mill at the bank of nearly every rock-salt pit, and in this the rock is ground to more or less fine powder when so required for shipment (*see* V. Buschman, *Das Salz dessen Vorkommen und Verwertung*, Willhelm Engelmann, Leipzig; also F. A. Fürer, *Salzbergbau und Salinenkunde*, Vieweg und Sohn, Brunswick).

The rock salt which is found in the neighbourhood of Stassfurt, in Prussia, is accompanied by deposits of a great variety of other minerals, especially those rich in potassium and magnesium. After boring through the Bunter sandstone, a bed of red clay and gypsum is encountered, under which lies the upper layer of rock salt, varying in thickness from 150 to 300 ft. For particulars of Stassfurt deposits. *v.* POTASSIUM, Vol. V. p. 372.

The salt deposits in the districts of Tarapaca and Atacama, in Chile and Peru, in great measure resemble those of Stassfurt. There is, however, one remarkable point of difference—the Peruvian beds contain large quantities of sodium nitrate or Chile saltpetre. The source of this nitrogen has long been a matter for discussion; but recent researches afford most probable explanations of its origin. It is noticeable that all these 'calichales' or 'salitrales,' as the spots are called where the 'caliche' or impure soda saltpetre is found, lie near to the coast, just inside the low-lying coast Cordilleras. The coast in this part of Chile is studded with small islands containing deposits of guano rich in ammonia, and this (in the form of very fine dust) is carried by the prevailing west wind far inland, and would doubtless fall

COMPOSITION OF ROCK SALT.

—	Cheshire	Wieliczka, white	Vic, red	Vic, grey	Hall, Tyrol	Marenes red	Virginia	Algeria	Berchtesgaden	Schwäbisc, Hall	Wilhelms-glück	Holsten, U.S.	Stassfurt	Cardona
Sodium chloride .	98.30	100.00	99.80	90.30	99.43	96.78	99.55	99.30	99.63	98.36	98.36	99.55	94.57	98.55
Calcium chloride .	—	—	—	—	0.25	—	trace	—	—	0.09	—	—	—	0.99
Magnesium chloride .	0.05	—	—	—	0.12	0.68	—	—	0.15	0.28	—	—	0.97	0.02
Sodium sulphate .	—	—	—	2.00	—	—	—	—	—	—	0.03	—	—	—
Calcium sulphate .	1.65	—	—	5.00	0.20	1.09	—	0.50	—	—	0.55	—	0.89	0.44
Magnesium sulphate .	—	—	—	—	—	0.60	—	—	—	—	—	—	—	—
Calcium carbonate .	—	—	—	—	—	—	—	—	—	—	0.52	—	—	—
Magnesium carbonate .	—	—	—	—	—	—	0.45	—	—	—	0.13	0.45	—	—
Alumina and ferric oxide .	—	—	—	2.00	—	—	—	0.20	—	—	0.53	—	3.35	—
Water .	—	—	0.20	0.70	—	—	—	—	—	—	—	—	0.22	—
Total .	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.12	100.00	100.00	100.00

into the saline lakes when in process of evaporation. The oxidation of this nitrogenous matter would doubtless readily take place under such climatic conditions as obtained when the salt deposits were formed.

The greater prominence of the more soluble potassium and magnesium salts in the nitre-bearing Chilean deposits furthers the supposition that they were formed from mother-liquors decanted from salt lakes further inland by volcanic upheaval. The theory that these mother-liquors, running down to the sea, were intercepted by the coast mountains is borne out by the fact that where there are no hills along the shore there are no nitre beds.

Manufacture of salt from brine.

The manufacture of salt has been carried on in England since the time of the Romans, who, there is little doubt, made it from brine. Brine is formed by fresh water reaching the surface of the rock salt, either at the outcrop of the strata or through a fissure in the overlying marl. In Cheshire it is pretty certain that the water gains admission at a higher level than the rock salt, for when the brine is first struck it rises up the shaft to a considerable height, in some cases nearly to the surface. The natural brine is, as would be supposed, only found on the top of the upper beds of rock salt. It is reached by means of bore-holes or by sinking a huge well or shaft, sometimes as much as 10 ft. in diameter. For the purpose of keeping water out, the shaft is lined with cast-iron cylinders carefully jointed together (see description of rock-salt mine shaft), or with timber backed with puddle. This shaft is carried down until the marl is reached, and then a bore-hole is driven until the brine is tapped. The top bed of rock salt in Cheshire is usually covered with a bed of marlstone, locally called 'the flag,' which is very hard and impervious to water. For a few feet below the flag the marl in which the rock head brine runs is of a granular structure, locally known as 'horse beans' or 'shaggy metal,' and is probably the remains of marl or other impurity originally combined with the rock salt, but left behind as the rock salt is dissolved into brine. On piercing the flag the brine rises into the shaft with great force. Common lift pumps are employed to raise the brine to the surface. They are suspended by a chain of rods depending from a rocking shaft and T bob at the top of the well. One engine, placed near the top of the shaft, generally works a pair of pumps. The brine is delivered into reservoirs which are lined with puddle-clay and brickwork.

The clay suffices to make them watertight, and the bricks, which are laid without mortar on the top of the puddle, keep it from being washed away. Very frequently, large wooden tanks are used as brine reservoirs. These are constructed of stout planks held together by wooden plugs (nails cannot be used on account of corrosion) and carefully caulked with oakum. The brine is distributed to the salt pans through pipes. In many places it was common until 20 or 30 years ago to employ pipes made out of the trunk of a tree bored out in the core and tapered at one end. The taper end fits into the core of the next pipe.

Such ranges are found to stand changes of

COMPOSITION OF BRINES.

100 parts of brine contain	Mars-ton	Wheelock	Droit-wich	Stoke Prior	Fried-richshall	Hall	Artern	Clemens-hall	Sulz	Syracuse, New York, U.S.A.	Stafford	Fleet-wood	Middles-borough	Winsford	Middle-wich	Northwich Bottom Mine	Schön-beck	Roden-berg
Sodium chloride .	25.222	25.333	24.97	25.492	25.563	25.717	25.267	25.902	23.473	21.710	24.850	24.980	24.930	25.460	25.110	25.790	9.623	5.173
Potassium chloride .	—	—	—	—	—	—	0.119	—	—	—	—	—	—	—	—	—	0.007	—
Magnesium chloride	—	0.171	0.05	—	0.005	—	0.421	—	—	0.136	0.168	0.046	—	0.214	0.171	0.093	0.083	0.166
Calcium chloride .	—	—	—	—	—	—	—	—	—	0.188	—	—	—	—	0.053	0.044	—	—
Potassium sulphate .	—	—	—	—	—	—	0.291	—	—	—	—	—	—	—	—	—	0.014	0.515
Calcium sulphate .	0.391	0.418	0.37	0.261	0.437	0.171	0.400	0.444	0.508	0.500	0.429	0.515	0.450	0.452	0.425	0.450	0.339	—
Sodium sulphate .	0.146	—	0.26	0.594	—	0.038	—	0.019	—	—	—	—	0.020	—	—	—	0.249	0.005
Magnesium sulphate	—	—	—	—	0.023	—	—	—	—	—	0.090	—	0.046	0.001	—	—	0.012	0.010
Calcium carbonate .	—	0.052	—	—	0.010	0.002	—	0.019	0.016	—	0.010	0.036	0.030	0.016	0.004	0.018	0.026	—
Magnesium carbonate	0.107	0.107	—	0.034	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Ferrous carbonate .	—	—	—	—	—	—	—	—	—	0.005	—	—	—	—	—	—	0.001	—
Total .	25.866	26.081	25.65	26.381	26.038	25.928	26.498	26.384	23.997	22.545	25.547	25.577	25.476	26.143	25.763	26.395	10.354	5.869

temperature better than iron ones. In Austria also there are many miles of such ranges of pipes. The strength of brine varies very greatly. It is, of course, dependent upon the volume of water which passes over the rock salt, the area of the surface over which it runs, and the length of time it is in contact with it. The table on the previous page shows the composition of brine in various places and countries.

In some countries where the brine is found too weak to make the ordinary method of evaporation a profitable one, recourse is had to a device to strengthen the brine by evaporation at the ordinary temperature. This is done by means of so-called graduation towers or houses (German, *Gradirhäuser*). They consist of scaffolding which encloses bundles of brambles or thorns, built up in regular walls. The weak brine is pumped up to the top, and carefully distributed by means of perforated troughs all over the summit of the pile. It then falls from twig to twig, and is divided into a fine shower on its way to the ground, thus exposing an immense surface to the action of the air or wind. At the bottom it falls into a collecting trough, whence it is returned to the top of the same or another tower until it becomes sufficiently concentrated. In time, the thorns become coated with a scale of calcium carbonate and sulphate, and then they have to be renewed. This incrustation is technically known as thorn-stone (German, *Dornenstein*). The graduation houses should be built lengthwise in the direction of the prevailing wind. The rapidity of evaporation depends upon the hygrometric state of the atmosphere. On rainy days graduation cannot go on. Experience shows that from May to August is the best season. It has been calculated that in ordinary good weather 60 kilos. (13 gallons) of water are evaporated in the course of 24 hours for every square foot of surface of the thorns. This method of evaporation is employed among other places at Moutiers in France, and at Nauheim, Dürrenberg, Rodenberg, and Schönbeck in Germany.

In some districts where rock salt is found the water does not naturally percolate to the strata, and therefore no brine is struck when borings are made. An artificial brine is readily prepared by turning a stream of fresh water down on to the bed of salt, and then pumping it up again as it becomes saturated with salt. The strong brine, being much heavier than water, collects at the bottom of the bore-hole, so the pumps are made to draw from the bottom, and are only run so long as the brine delivered keeps up to strength. The yield of such a bore-hole, of course, depends upon the area of the surface of the rock salt which the water can act upon, and this it will be seen is always increasing. The whole of the brine evaporated in the Middlesbrough district is made in this way. Water from the sandstone strata is allowed to flow down the well outside the pump barrels, and thus solution of the salt takes place at the top of the bed, by which a cavity is formed. As the brine is pumped from the bottom of the cavity more water flows down, and thus the cavity becomes larger and its productive power is increased. As the specific gravity of brine is about 1.2, the column inside the suction pipe rises to $\frac{5}{6}$ of the height of the water column outside.

The removal of these subterranean beds of rock salt by the agency of water occasions in some districts very serious consequences. In carefully worked mines the pillars which are left are ample to support the superincumbent strata so long as the mine is kept dry. But if, by any chance, water finds its way in large quantities into a salt mine the pillars are rapidly dissolved, and a large area of roof is left without any support. Then a subsidence of the land, occurring more or less rapidly, is sure to take place. The water which naturally finds its way down to a rock-salt bed may run for miles along its surface, and so gradually remove an ever-increasing layer of the salt. If there is no natural outlet the solution of salt ceases when the water becomes saturated; but if the brine is pumped out for manufacturing purposes an equivalent volume of fresh water is induced to flow in, and so the destruction of the salt bed is greatly intensified. This constant removal of the support causes as constant a subsidence of the outlying lands, and it is by no means uncommon in the brine-pumping districts for pieces of land to sink at the rate of a foot a year (*see Subsidence in the Salt Districts of Cheshire: their History and Cause*, Thos. Ward, Trans. Manchester Geol. Soc. vol. xix. part vii. 1886-7).

The manufacture of salt from brine is essentially a very simple process. It is merely necessary to evaporate a certain amount of water and collect the salt which deposits. This is effected either by artificial heat or by the heat of the sun. When the former is employed, it is obvious that the best process is that which secures the greatest evaporation for the smallest expenditure of fuel. Until recently, the method universally adopted was to use an open shallow pan and heat it by a fire placed underneath. The Romans in Cheshire used leaden pans which contained only a few gallons of brine; but the modern pans are made of wrought iron plates riveted together and frequently hold as much as 50 cubic metres. Apart from this variation in the construction and size of pans, the process has been little affected by the various and numerous patents taken out for improvements until about 1892.

The following is a list of some of the most important of the patents:—

In 1764 John Baker patented a salt-pan covered over from end to end with a brickwork arch, and so arranged that the hot gases which had already passed under the pan should be drawn over the surface of the brine.

In 1772 Daniel Scott and John Mackay proposed to arrange pans three high, and conduct the steam from the bottom boiling pan through false bottoms under the other two.

In 1801 James Manly patented a process for purifying brine. He proposed to heat, in order to remove part of the impurity, and then to add sodium carbonate to it.

In 1806 Richard Tomkinson designed a salt-pan which contained a hollow iron cylinder running right down the centre and out at the other end. The middle of the pan was deeper than the sides, and the cylinder was supported so that the brine surrounded it at all times. The fire was placed in the cylinder at one end of the pan.

In 1808 William Steel patented a plant

consisting of three separate vessels. The boiling vessel was provided with an air-tight cover, and the steam from it was conducted under a second vessel. The hot air and flame from the flue of the first was taken under a third vessel.

In 1824 W. A. Jump and W. Court proposed to heat the first brine in metallic pipes, placed in the flues under the pan.

In 1831 W. A. Jump patented a pan provided with mechanical rakes to draw the salt to the side of the pan.

In 1833 W. Newton proposed to blow hot air through the evaporating brine.

In 1838 Joseph Hall patented a circular revolving pan. The salt, as it formed, was scraped by means of a fixed rake into a pocket at the circumference of the pan. He also described a semicircular pan with a reciprocating motion. He claimed that in such pans the heat was more evenly distributed and the wear consequently less.

In 1839 Edward Law patented a machine for evaporating brine by exposing an extensive surface to the action of a brisk current of air. The apparatus consisted of an upright shaft or axis carrying ten frames covered with canvas. These were constantly moistened with brine while the machine was turned rapidly on pivots.

In the same year (July 16, 1839, No. 8155) an important step was taken by John Reynolds, who invented a process for improving the manufacture of salt by 'causing the steam produced by boiling brine or salt water in a closed vessel to transfer its heat to and thereby boil brine or salt water in a second closed vessel, so that the steam from such second closed vessel may in like manner transfer its heat to brine in a third vessel, and so on, by maintaining in each of a series of closed vessels in which brine is subjected to evaporation such relative pressure as will cause the respective boiling-points of the brine contained in each to be lower from the first to the last of the series, so that the steam or vapour produced from the brine in each vessel may be condensed in a vessel of thin metal immersed in the brine of the next succeeding vessel. The graduations of pressure may be obtained either by diminishing a pressure superadded to that of the atmosphere, or by diminishing the pressure of the atmosphere alone.'

In 1855 L. J. F. Margueritte proposed to precipitate salt from a solution by passing hydrogen chloride into it.

In 1864 D. Hall and A. L. Roosen patented the application of surface heating for the evaporation of brine. The pan was covered with a brick arch, and the heat from the furnace was allowed to pass over the surface of the brine, and then afterwards, together with the steam evolved, under an ordinary open salt-pan.

In 1889 Alberger, Williams and Alberger patented a combination of tubular steam heaters and a circular open pan termed a 'grainer.'

In 1893 C. Hirzel proposed to freeze brine at -20° and separate the hydrate.

In 1898 Vis patented the use of calcium chloride to prevent the calcium sulphate in brine scaling a pan.

In 1899 Vis patented an arrangement for preventing scaling in vacuum apparatus.

In 1899 Duff patented a special arrangement of multiple effect vessels.

In 1900 Vis proposed the purification of brine by electrolysing it until caustic soda was formed in sufficient quantity to precipitate the calcium and magnesium salts when treated subsequently with carbon dioxide.

In 1902 Sachse and Kaufmann patented apparatus for keeping the tubes of a vacuum evaporator clear by causing a weighted chain to bump over the top tube plate.

In 1903 Trump took out a patent for vacuum apparatus containing a circulating pump which, by causing the crystals and mother-liquor constantly to be returned to the evaporator, allowed the crystals to grow larger and at the same time tended to prevent the formation of scale by scouring action.

In 1903 Tee patented a process for making white salt by melting rock salt, blowing heated air through the liquid, allowing impurities to settle and then drawing off the clear salt into vessels to cool.

In 1908 Malcolm and Munton patented a process for preventing scaling in vacuum evaporators by purifying the brine. The magnesium salts are removed by adding partially electrolysed brine (*i.e.* brine containing some caustic soda) to the raw brine and then the calcium salts are precipitated by the addition of more electrolysed brine and treatment with flue gases (*i.e.* CO_2).

In 1910 the Salt Union, Malcolm & Munton, took out a patent (No. 13415) for a process for making common salt. This involves the use of steam-driven dynamos for generation of electricity and employment of the exhaust steam in vacuum evaporators. Electric current is used for the purification of brine, as specified in the earlier patent of Malcolm & Munton, the chlorine being employed to make bleaching powder, and the surplus electricity is utilised to form a district supply.

In 1911 Webster and the International Salt Company patented a process for purifying salt by blowing air through a flowing molten mass and subsequently granulating the salt by agitating it whilst cooling.

Of late years the greatest improvements which have been made in the manufacture of salt have been in the direction of the triple effect apparatus described by Reynolds in 1839.

The cost of fuel is so large an item in the cost of production of salt that any economy effected in its use materially increases the margin of profit. With the ordinary open pans, 1 ton of fuel (slack with 15-20 p.c. of ash) will make from 2 to 2.5 tons of salt; but a well-constructed triple effect plant will yield 5-6 tons of salt per ton of fuel. In addition to giving greater economy in consumption of fuel, these vacuum pans have a much larger production capacity than the ordinary pans.

While, with a direct-fired pan of large size, it is considered good to get 15 tons of salt per 24 hours, it is not uncommon for a set of multiple effect vacuum evaporators to yield 500 tons per day. The evaporators are constructed with a central heating portion, a dome-covered upper part and a conical lower portion communicating with a salt receiver.

Heat is applied to the vessels through tubes

which prevent the brine from coming into actual contact with the heating medium. Steam or any hot gases, such as flue gas or exhaust

from gas engines, can be employed for heating the first vessel in the series. The steam which is evolved from the boiling brine in the first

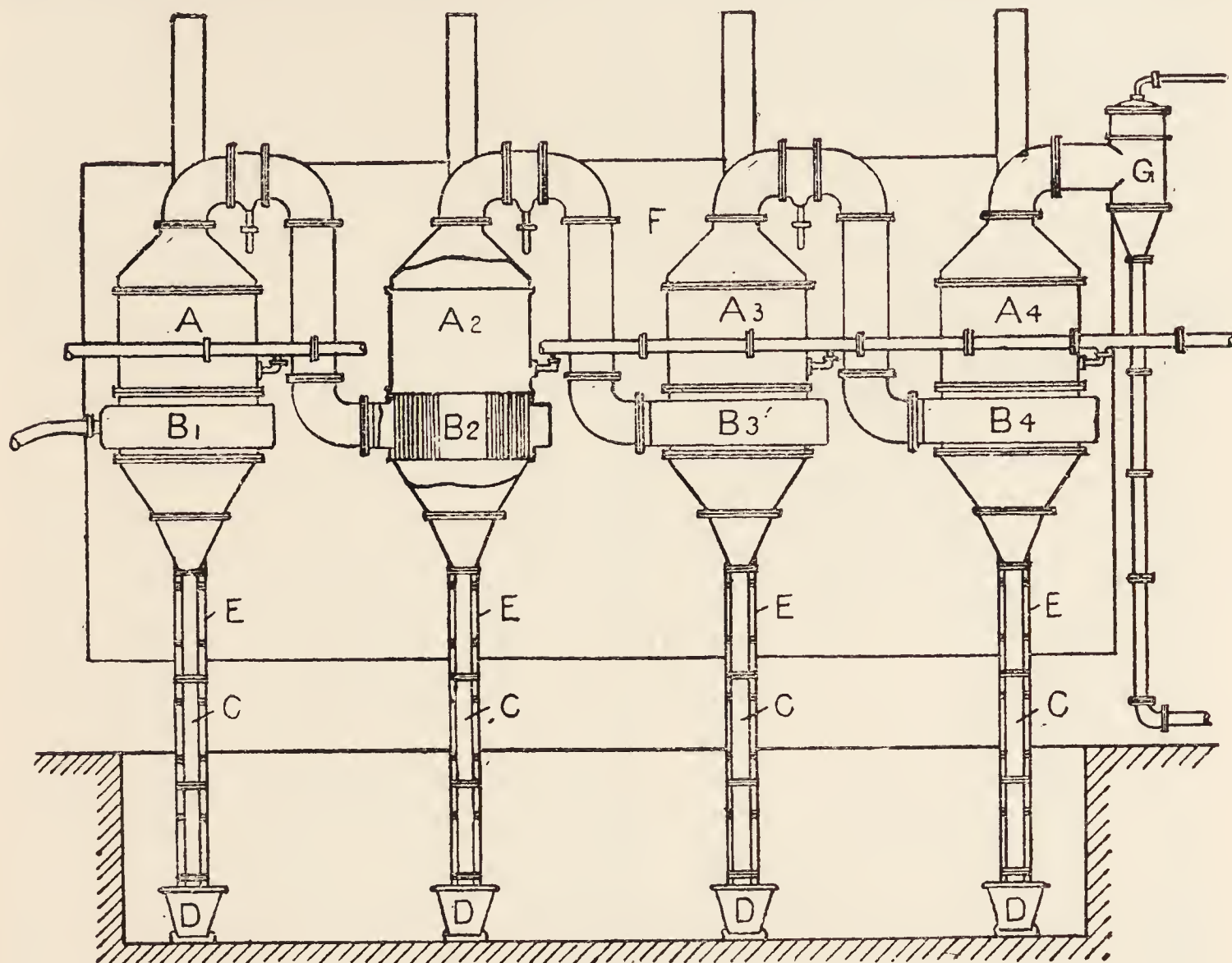


FIG. 23.

vessel is employed for heating the second of the series, and that from the second serves to heat the third. Where a fourth vessel is employed, the heating is effected by steam from the third. The steam evolved from the last vessel of the series passes to a vacuum engine after a condenser. With this arrangement, evaporation takes place in each vessel at a lower pressure, and therefore at a lower temperature, than in the preceding vessel, so, while the pressure in the first may be little below atmospheric, that in the last is a high vacuum.

To facilitate the removal of salt without interruption of the process of evaporation, it is usual to make a long leg to the evaporators so as to maintain a column of brine equal to the vacuum and allow the crystals to fall into a receptacle which lutes the bottom of the leg. It is common to provide this with an elevator and so remove the salt as it forms to a storage hopper.

Fig. 23 shows the arrangement of a typical multiple effect plant. In this plan four vessels are shown, marked A1, A2, A3, and A4. The heating chambers are marked B1, B2, B3, and B4. That of B2 is shown in part section to illustrate the arrangement of tubes through which the brine circulates. The long leg C of each vessel terminates in a boot at an elevator bottom, and the salt is raised by the elevators E to the receptacle F. G is a condenser for producing vacuum by the condensation of steam.

Fig. 24 shows an end view of the same plant.

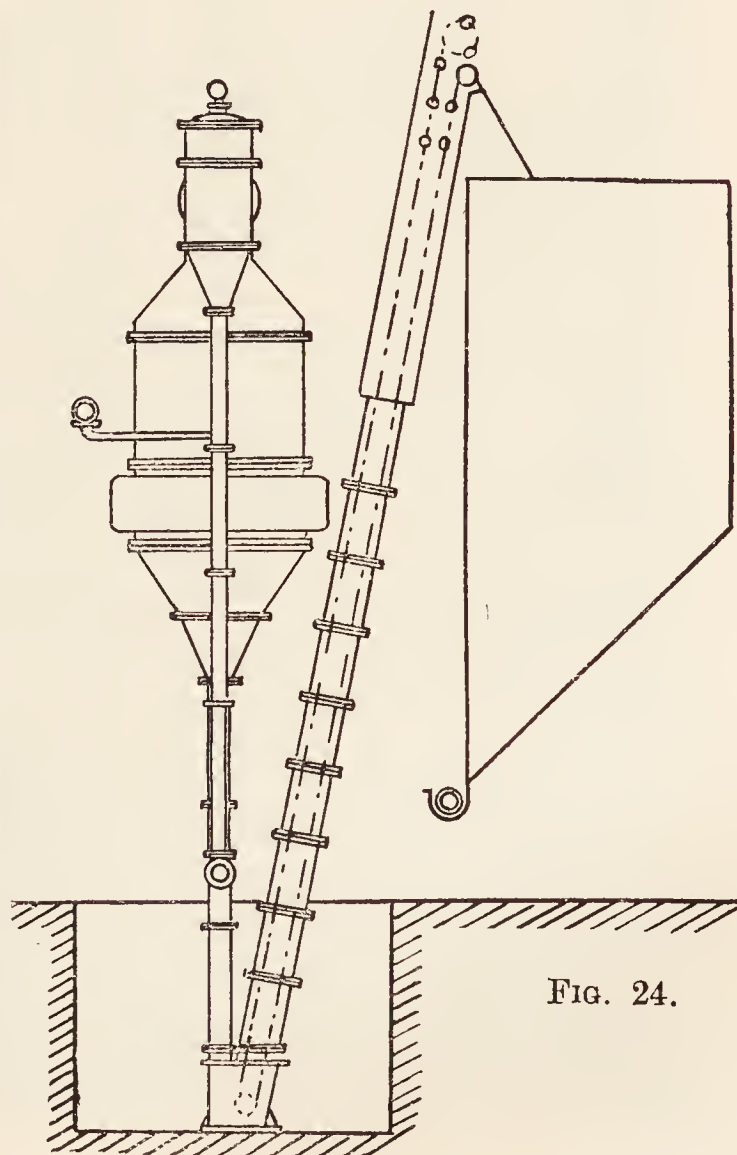


FIG. 24.

Each vessel has a separate brine-feed pipe from a common main.

Fig 25 below illustrates another form of plant where the vessels are placed at different heights, so as to give a length of leg in proportion to the vacuum in the vessel.

This process has rendered the manufacture of salt remunerative in places where heat was in some form or other being wasted. One of its first applications was in utilising the exhaust steam from the lumber mills of Michigan, and latterly it is being found suitable for making use of the steam from turbines employed for generating electricity. The great source of trouble in working the process is the impurity of ordinary brine. The calcium sulphate, which

every natural brine contains, separates in the form of scale on the tubes. This scale, containing anhydrite, and a large quantity of salt, has to be constantly removed because it seriously interferes with the transfer of heat.

Many devices have been tried to overcome this difficulty. Some of the most obvious are those which deal with the partial purification of the brine prior to its use in the evaporators. Other mechanical ones have been fairly successful, notably that patented by Trump in 1903. The best, however, appears to be the addition of calcium chloride to the brine during evaporation, as suggested by Vis in 1898. This causes precipitation of the calcium sulphate in the form of small crystals that mix with the salt and does

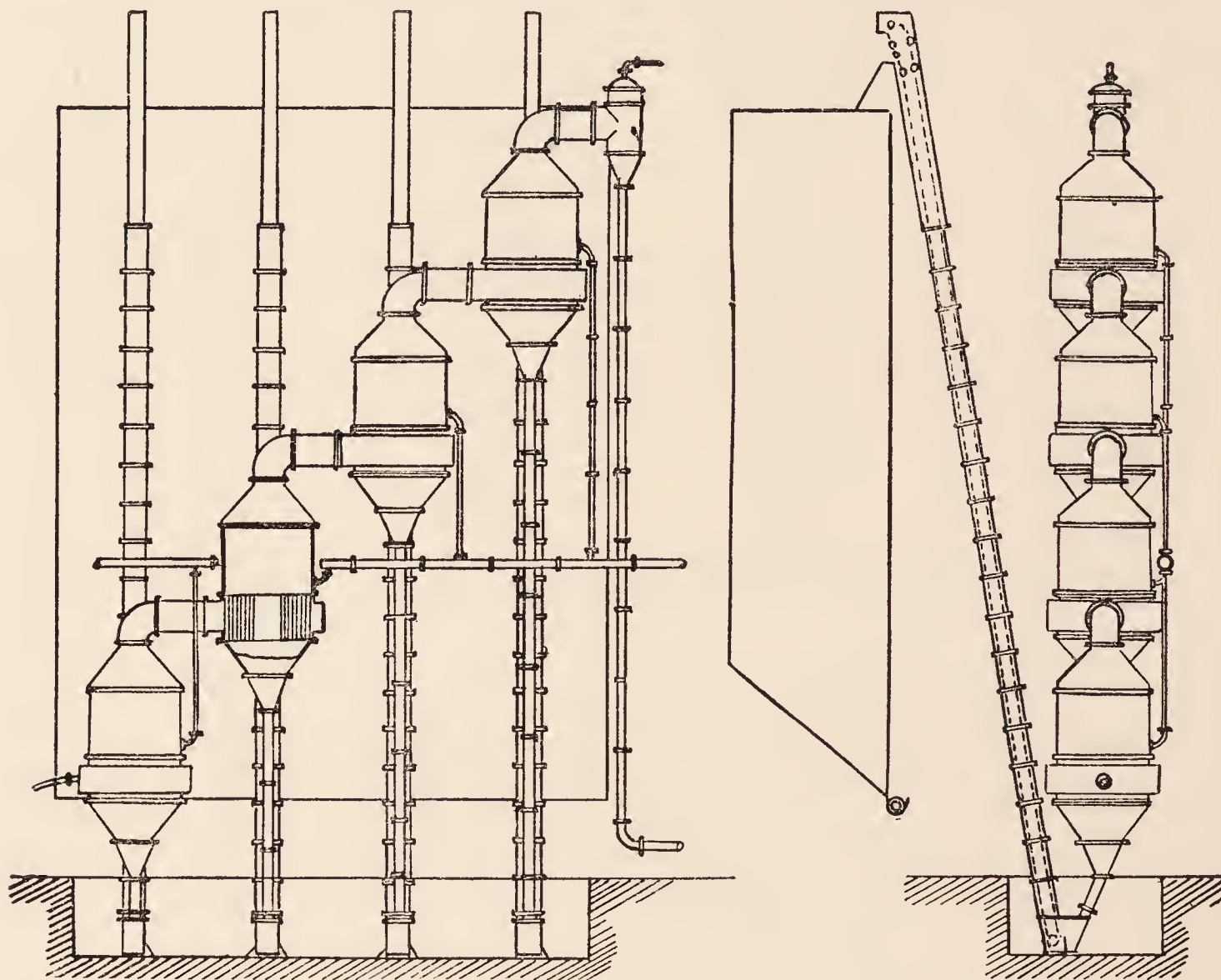


FIG. 25.

not allow scale to form on the tubes. The salt, on withdrawal from the apparatus, is washed free from calcium chloride with fresh brine. The washings are sent with the brine fed into the evaporators and so the calcium chloride is used over and over again.

Fig. 26 gives a view of the triple effect evaporators erected by the Salt Union at Weston Point, Cheshire. The vessels are 26 ft. 6 ins. diameter and 66 ft. high. The steam from the third evaporator passes into a barometric condenser 10 ft. diameter and 62 ft. high. This is capable of dealing with $26\frac{1}{2}$ tons of steam per hour and uses 330,000 gallons of water for condensing. The plant is designed to produce from 450 to 500 tons of salt per day. Steam direct from the boilers is employed for running high-speed engines to generate electric current, and the exhaust steam is used for heating the vacuum evaporators.

Salt makers experience one difficulty in working vacuum plant, and that is, the grain of the salt produced is always fine. Large crystals cannot be formed under such violent agitation, and, when they are required, the manufacturer has to revert to the old-fashioned open pan.

In the ordinary process of manufacturing salt the brine is run into a shallow pan, which is heated from below, and is made of such a shape as will expose as much surface as possible both to the action of the fire and of the air. The oldest pans of which there is any record were made of sheet lead, and were only about 3 ft. square and 3-4 ins. deep, holding little more than 15 gallons. These so-called 'leads,' when filled, were set aside in a warm place or on a hot flue, until the brine deposited its salt. About the middle of the seventeenth century iron pans superseded the leaden ones.

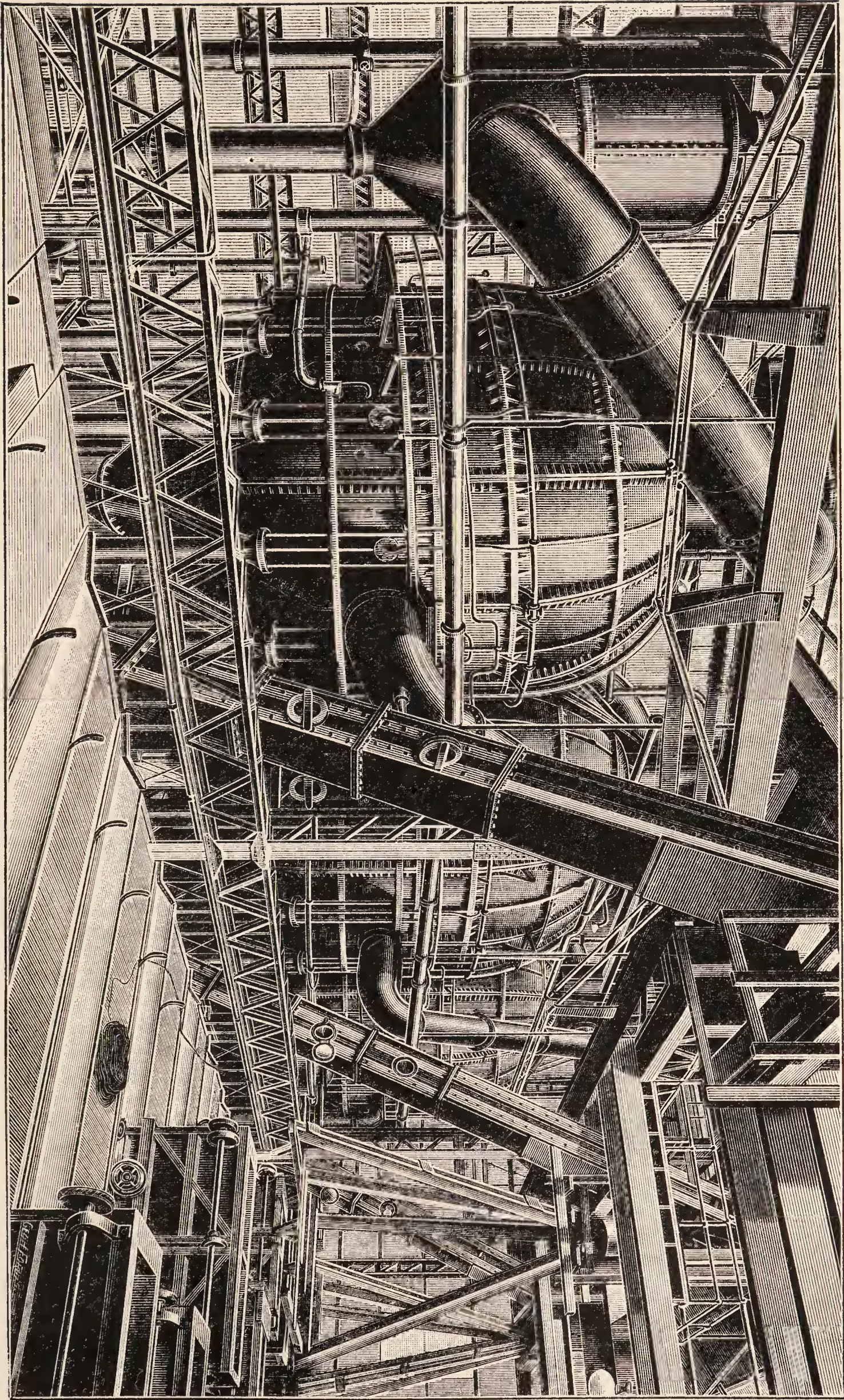


FIG. 26.

Writing in 1748, Brownrigg describes pans then-in use as being made of 'plates of iron joined together with nails and the joints filled with a strong cement. Strong iron hooks hang down from beams of iron fixed across the pan and are linked to other hooks on the bottom of the pans and thus prevent it from bending down' (The Art of Making Common Salt).

In 1765 the largest pans used at Northwich

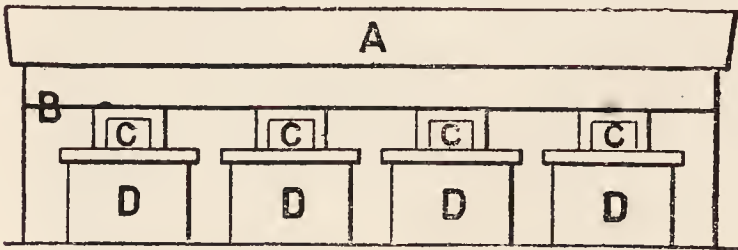


FIG. 27.—SETTING OF SALT-PANS.

A. The salt-pan. B. The front wall or fore-bye. C, C, C, C. The fireplaces. D, D, D, D. Ash holes.

were 20 ft. long by 9 or 10 ft. wide. At the present time the smallest employed are 25 ft. long by 20 ft. wide and 15 ins. deep, while some of the pans used for making coarse salt are 70 ft. long by 25 ft. wide and 18 ins. deep.

The pans are placed upon brickwork, which serves for a support and also forms the walls of the flues. The fireplaces are placed in the front, and vary in number from 2 to 4,

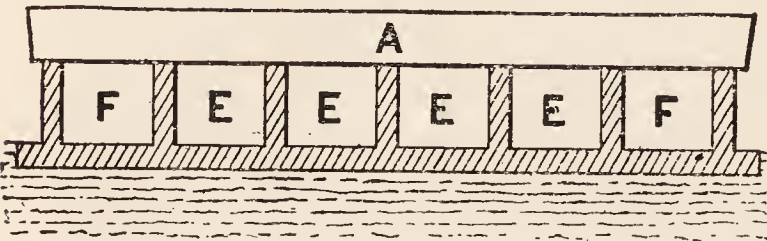


FIG. 28.—SETTING OF SALT-PANS.

A. The salt-pan. E, E, E, E. The flues.

according to the size of the pan and the work it has to do. The flues are frequently carried straight from front to back of the pan. In some pans the portions marked F in Figs. 28 and 30 are shut off from the flues in order that when the salt is raked up to the side, previous to drawing, it does not cause super-heating of the pan plates. Fig. 27 shows the front view of a salt pan; Fig. 28 is a cross section at the break

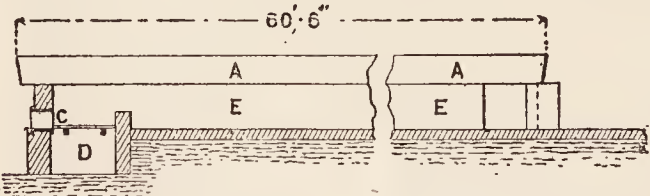


FIG. 29.—SETTING OF SALT-PANS.

A. The salt-pan. C. The fireplace. D. Ash hole. E. Flue.

shown in Fig. 29; Fig. 29 is a longitudinal section; Fig. 30 is a plan of the flues.

The pans are made of wrought-iron plates carefully riveted together like boilers. The plates which lie directly over the fires are made of greater strength than the rest of the pan, on account of the greater wear which they have to stand. As these plates have to be renewed more frequently than any others, they are made smaller, and are so arranged that they can readily be cut out (see Fig. 31). Each set of fire-plates A, A, A, A, is separated from its neighbours

by a midfeather plate B, B, which rests upon the wall dividing two fireplaces. The two outer sets are separated from the side of the pan by a similar long plate. The bottom and sides of the pan are joined by means of an angle iron, to which each is firmly riveted (Fig. 32).

As above stated, the plates A which lie in

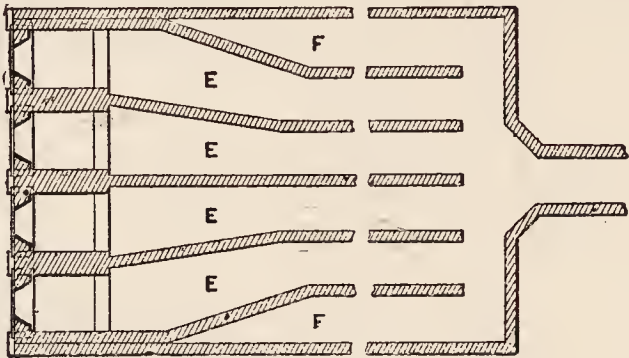


FIG. 30.—SETTING OF SALT-PANS.

E. Flues. F. Blank spaces.

the vicinity of the fires are subjected to the greatest wear. When they become over-heated they sink and stretch, and, in so stretching, they tear the plates c at the front of the pan. It is obvious that the removal of the front plate would necessitate frequent interference with the angle iron, and this would entail a greater expenditure of labour; therefore it is found

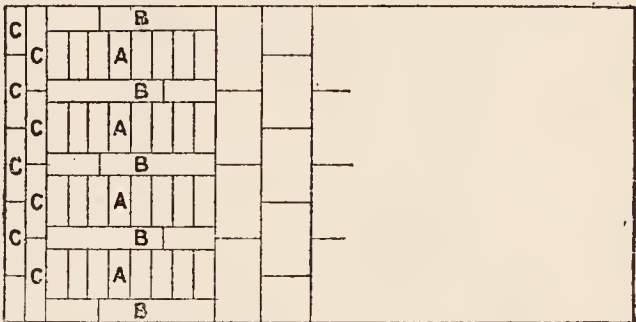


FIG. 31.—PLAN OF SALT-PAN, SHOWING ARRANGEMENT OF PLATES.

advisable to place two rows of plates along the front. All the plates used in the neighbourhood of the fires are $\frac{3}{8}$ in. thick, while those employed for the back parts are $\frac{1}{4}$ in. Some French pans have the fire-plates raised towards the centre above the level of the rest of the pan (see Fig. 35), in order that the salt, when formed, may float off the fire-plates. Salt-pans should

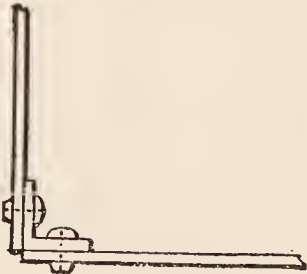


FIG. 32.

be made to extend about 1 ft. or 1 ft. 6 ins. beyond the front wall, in order to keep the angle iron well out of the fires. They are also made to overlap the side walls by about 6 ins., for the double purpose of keeping the angle iron clear of the flues, and for allowing what is known as toe-room for the man who draws the salt out of the pan. If the drawer can place his toe under the pan, he is able to get his leg flat against the side of the pan. This affords him greater power in stooping over the pan, and prevents him wearing the skin off his knee.

The best method of setting the pan on the side walls is to build up a 9-in. wall, and make the top course of bricks only $4\frac{1}{2}$ ins. deep (see Fig. 33).

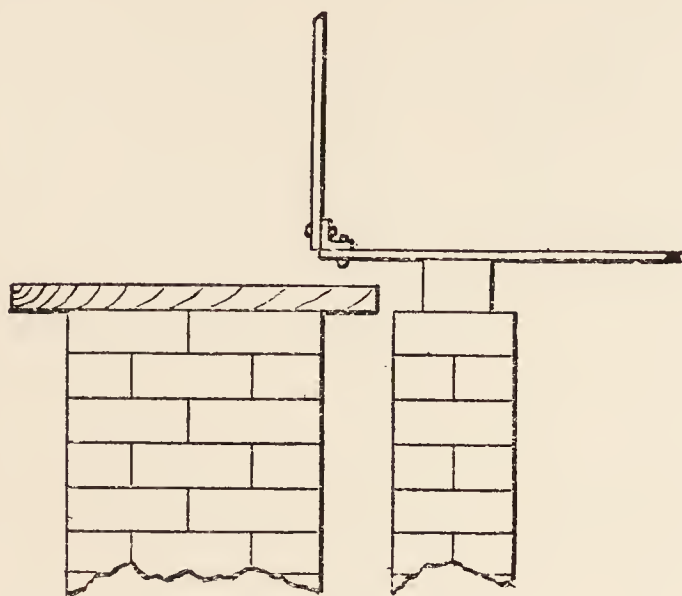


FIG. 33.

What is technically known as the 'standing side' consists of a gangway of 2-in. planks about 2 ft. wide, which runs the entire length of the pan, on a level with the top of the 9-in.

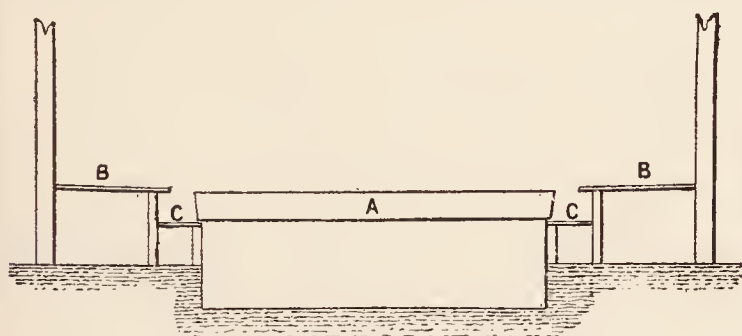


FIG. 34.

A. Salt-pan. B, B. The hurdles. C. Standing aside.

side wall. On both sides of the pan, and often across the back, there runs a platform composed of 2-in. planks well jointed together, and caulked with oakum. These stages are technically known as the 'hurdles,' and serve for a

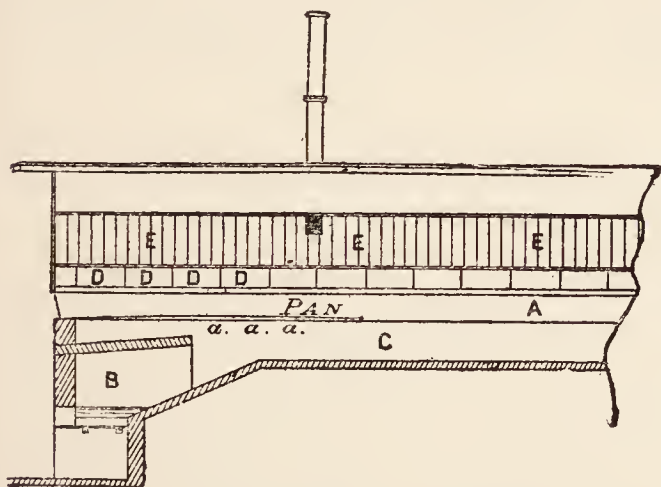


FIG. 35.—LONGITUDINAL SECTION OF A FRENCH SALT-PAN, SHOWING SHAPE OF PAN AND ARRANGEMENT OF WOODEN COVER.

A. Salt-pan. a, a, a, Raised fire-plates. B. Fireplace, C. Flue. D, D, D, &c. Movable doors in cover. E, E, E. Cover forming hurdles.

receptacle for the wet salt freshly drawn from the pan. They have a fall towards the centre or half-length of the pan, and are bordered on the pan side by a gutter in order that the brine which drains from the salt may run back into the

pan (Fig. 34). It is customary on the Continent to cover in the salt-pans with a wooden shelter, provided with an upright shoot to take off the steam. In such cases this cover serves instead

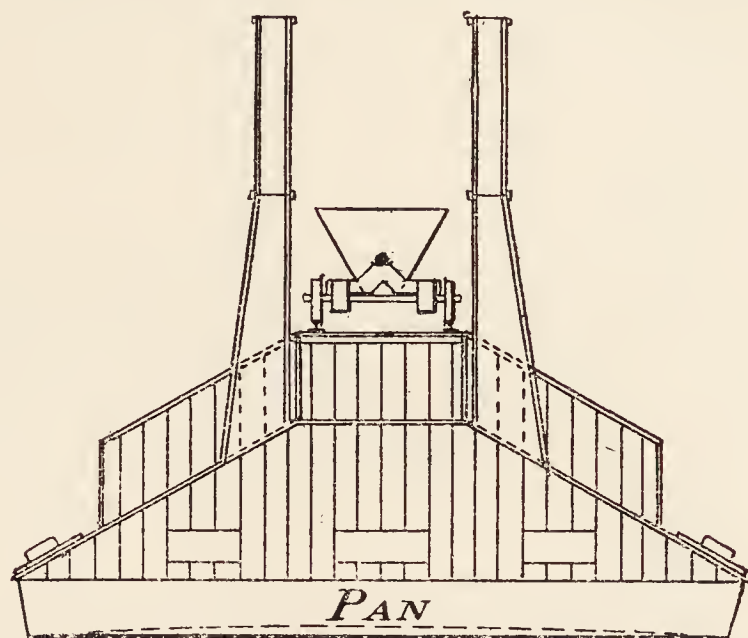


FIG. 36.—FRONT VIEW OF A FRENCH SALT-PAN, SHOWING CHIMNEYS TO CARRY OFF THE STEAM.

Dotted line shows curve of the pan over the fires.

of the hurdles, and it possesses the distinct advantage that the heat from the pan serves in a great measure to dry the salt. In some Continental works a tramway runs down the centre

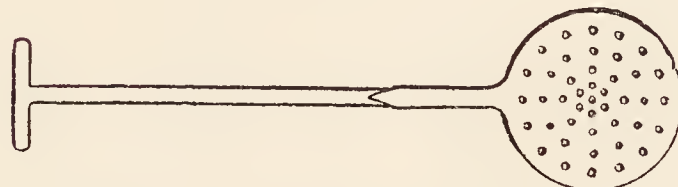
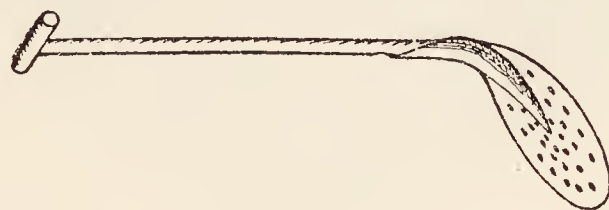


FIG. 37.

of this wooden cover, and the salt is taken off in trucks (see Figs. 35 and 36).

Fine-grained or lump salt.—Fine-grained salt is made in the smallest-sized pans. These

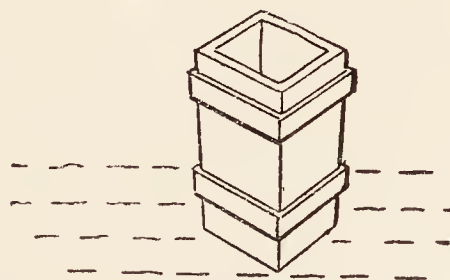


FIG. 38.—A BOX FOR LUMP SALT.

are 25-35 ft. long and 20-24 ft. wide and 15-18 ins. deep. The brine is boiled and reaches the temperature of 226°F. or 107.5°C. As the salt forms it is raked off the fire-plates to the side of the pan from time to time. Twice or three times in 24 hours the salt is drawn from the pan.

The salt is lifted out of the pan on a perforated sort of shovel, known as a 'skimmer' (Fig. 37). As it is drawn out of the pan it is placed either in wooden boxes (Fig. 38) standing

on the hurdles, or thrown on to the hurdles in bulk. As it cools in the boxes the hot brine which it contains crystallises, and suffices to cement the whole together into a solid mass. This is knocked out of the box and placed in the stoving chamber to dry. This hot room is generally heated by the waste heat from the flues of boiling pans. The fine table salts are prepared by crushing and grinding the lumps after drying.

Common salt.—The name 'common' is given to that grain of salt which is made for use in various manufacturing operations. It is made at a temperature of 160° – 180° F., or 61° – 82° C., in pans 45 ft. long by 25 ft. wide and 18 ins. deep. The salt is raked off the fires about every 2 hours, and drawn out of the pan every 24 or 48 hours. After draining on the hurdles for some hours it is shipped off in railway waggons.

Fishing salt.—Fishing salt is a coarse-grained variety manufactured for the fish-curing trade. It is made at a temperature of 100° – 140° F., or 37.7° – 60° C., in pans 50–60 ft. long by 24–25 ft. wide and 2 ft. deep. The salt is drawn out once a week or once a fortnight, according to the grain required. These pans are

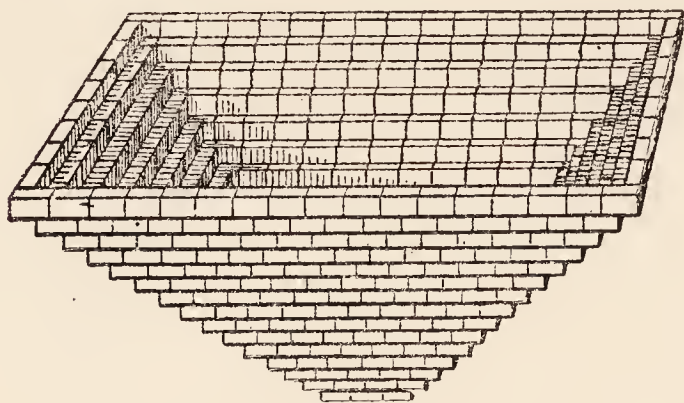


FIG. 39.

often heated by the flue gases from boiling-pans. A little alum is added to the brine to harden the crystals of salt.

Bay salt.—Bay salt is the coarsest-grained salt manufactured. The pans employed are very large, sometimes even 140 ft. long by 25–30 ft. broad. The temperature of the brine is kept at about 100° – 120° F. The salt is drawn every 3 weeks or month.

The salt manufacturer frequently manipulates his brine in order to obtain the exact grain of salt that he requires. The addition of gelatin, glue, or any kind of grease causes the salt to form in very small crystals, whilst the addition of alum has the opposite effect. The operation of adding such substances is technically known as 'poisoning the pan.' Alum is employed in the manufacture of the variety of salt known as 'hopper salt.' It causes the salt to crystallise in hollow cubes, and as these float about before falling to the bottom of the pan they become surrounded by others, and gradually form into the shape of a shoot or hopper (Fig. 39)

Natural brine is seldom a solution of pure sodium chloride, but generally contains other salts in solution, as will be seen from the foregoing analyses (p. 200). Certain of these substances separate out during the process of evaporation, and not only render the salt impure, but give trouble in the pan. If the brine contains calcium bicarbonate, the application of heat

produces a precipitation of calcium carbonate. When this occurs in a salt-pan the calcium carbonate (which is almost always accompanied by oxide of iron) deposits on the top of the fire plates, and forms what is technically called 'sand scale.' This has to be broken from time to time with a blunt pick and fished out of the pan, otherwise the plates would get red hot and burn away. When a pan begins to leak, the brine often crystallises as it drops into the flue, and forms a stalactitic mass, which is locally called a 'cat.' This is not the only trouble caused by a leaky pan, for, in addition, hydrochloric acid is frequently formed, through the decomposition of sodium chloride by sulphur dioxide in the presence of water. The sulphur dioxide is generated by the combustion of small quantities of pyrites in the fuel. All British salt works are now under Government inspection, and the chimney gases are tested from time to time by the inspectors.

If brine contains calcium sulphate, it deposits it when heated. This falls to the bottom of the pan, and forms a scale which frequently contains a large quantity of salt. It sometimes accumulates to a thickness of 4 ins. and is known as 'pan scale.' On account of the growth of scale and the consequent decreased efficiency of the pan, it becomes necessary after working for a given time to run off all the liquid from the pan and remove the scale. This operation is termed 'picking' the pan.

Solar salt.—In some places, where the natural brine is so weak or fuel is so scarce that evaporation by artificial heat is not remunerative, salt is made by exposing the brine to the rays of the sun in large wooden pans resting on the ground. Such pans are frequently provided with movable covers which are pushed aside in fine weather and drawn over if rain comes.

Along the sea-coast of countries which possess a dry climate or habitually experience a hot summer, salt is made by solar evaporation of sea-water.

A large piece of land, slightly below high-water mark, is levelled and surrounded by a wall or bank. The ground is, if necessary, puddled with clay to make it water-tight, and the enclosed space is divided into compartments by internal walls. Sea-water is admitted at high tide, and, after being allowed to deposit any solid matter it may contain, is run from compartment to compartment until salt crystallises out. This is then raked together into heaps and allowed to stand while the more deliquescent salts, such as magnesium chloride, run away. These salt gardens (German, *Salz-Gärten*) are freely worked in Portugal, Spain, France, Austria, Corsica, Italy, Cyprus, Smyrna, California, China and in India, and produce very large quantities of salt. The product is naturally much more impure than that made from brine derived from rock salt.

Within recent years the production of 'solar' salt has greatly increased. In the Montpellier district of France there are numerous salins along the coast line from Hyères to Cette, a stretch of 140 miles. The total area of evaporation surface utilised is well over 4000 acres, and under normal conditions the district produces annually 150,000 tons of salt.

Solar salt works are fairly common along the

shores of San Francisco bay, especially on the eastern side. These have an evaporation area of over 8000 acres and a productive capacity of 200,000 tons of salt per annum. Some of the works make refined table salt by dissolving crude salt in fresh water and, after purifying the solution with lime and carbonate of soda, evaporating it in multiple effect vacuum pans.

The world's output of salt.—According to Commerce Monthly, the world's production of salt in 1920 was about 18,700,000 tons, compared with approximately 17,200,000 gross tons before the war of 1914. Whereas the output of the United States has increased from 4,300,000 tons in 1913 to 6,107,000 tons in 1920; that of the United Kingdom declined from 2,248,000 to 2,158,000 tons during the same period. The output for other countries was as follows, the figures for 1913 being given in parentheses: Russia, 539,000 (1,910,000); Germany, 2,887,000 (1,888,000); France, 1,230,000 (1,262,000); Japan, 580,000 (610,000); Austria, 79,000 (Austria-Hungary, 585,000); Spain, 974,000 (59,000). India produced 1,764,000 tons in 1919 compared with 1,299,000 tons in 1913 (J. Soc. Chem. Ind. Auf. 1923, 835).

Production of salt in the United States in 1922 increased by 36 p.c. in quantity and 12 p.c. in value, to 6,792,849 short tons valued at \$27,464,838, compared with 4,981,154 tons valued at \$24,557,966 in 1921. In 1922 the number of operating plants was 104, a gain of 14. Sales of rock salt in 1921 and 1922 were 1,472,576 short tons (\$6,693,923) and 1,947,124 tons (\$7,489,644) respectively; of evaporated salt 1,931,243 tons (\$16,846,963) and 2,276,683 tons (\$18,472,759); pressed salt blocks 117,739 tons in 1921 (\$1,275,483), and 172,682 (\$1,554,429) in 1922. Imports in 1921 and 1922 amounted to 93,095 tons and 111,710 tons respectively, compared with exports during the same years totalling 109,563 tons and 334,989 tons respectively.

The output of calcium chloride was 23,672 tons (\$510,723) in 1921, and 33,067 tons (\$571,326) in 1912 (J. Soc. Chem. Ind. 1923, 42, 995).

The mother-liquors are comparatively rich in bromides of calcium and magnesium, and are sometimes employed for the extraction of bromine.

The output of bromine was 711,953 lbs. in 1921, and 1,005,174 lbs. in 1922, an increase of 41 p.c. in quantity, but a decrease of 13 p.c. in value compared with the previous year. The wholesale price of bulk bromine in 1922 was 20 to 21 cents per lb. from February until about the middle of March, then increased to 27 to 28 cents until the end of the year. Bromine had not been imported into the United States for several years prior to 1921, when imports of 300 lbs., valued at \$84, were reported. In 1922 imports were 1094 lbs., valued at \$339. Cf. Art. BROMINE, Vol. I. 688.

In some cold countries, such as Russia and Sweden, salt water is allowed to freeze, and the ice, which consists of nearly pure water, is removed. By repeating this several times, a mother-liquor is obtained which is sufficiently strong to boil down. The salt obtained does not contain more than 75–85 p.c. of sodium chloride.

Properties of sodium chloride. Poggiale (Annales de Chimie et de Physique [3], 8, 469)

gives the following data for solubility of sodium chloride in water:—

Temp.	S.	Temp.	S.
−15°	32.73	+40°	36.64
−10	33.49	50	36.98
−5	34.22	60	37.25
0	35.52	70	37.88
+5	35.63	80	38.22
9	35.74	90	38.87
14	35.87	100	39.61
25	36.13	109.7	40.35

Coppet (Annales de Chimie et de Physique [5], 30, 411) gives S. above 20° to 109°=34.359 + 0.0527 t.; Gerlach (Fresenius' Zeitsch. anal. Chem. 8, 281) gives the following data:—

Sp.gr. NaClAq at 15°.			
1 p.c.	1.00725	10 p.c.	1.14315
2 „	1.01450	11 „	1.15107
3 „	1.02174	12 „	1.15931
4 „	1.02899	13 „	1.16755
5 „	1.03624	14 „	1.17580
6 „	1.04366	15 „	1.18404
7 „	1.05108	16 „	1.19228
8 „	1.05851	17 „	1.20098
9 „	1.06593	18 „	1.20433

1000 c.c. of NaClAq saturated at 15° contain 318.479 gr. NaCl and 888.669 gr. water (Michel A. Kraft, J. 1854, 296). NaClAq containing 29.4 to 29.5 p.c. NaCl boils at 109.25° (at 760 mm. pressure) and freezes at −21.3° (Karsten, Salinekunde, Berlin, 1847, 2, 38). The following freezing-points are given by Karsten (*l.c.*) for NaClAq (*cf.* Rüdorff, Poggendorff's Ann. Phys. und Chem. p. 114, 63, and de Coppet, Ann. Chim. [4], 25, 509):—

P.c. NaCl	F.p.	P.c. NaCl	F.p.
2	−1.32°	16	−11.69°
4	−3.024	20	−14.44
6	−4.52	22	−15.78
8	−5.99	24	−17.11
10	−7.44	26	−18.42
12	−8.88		

For freezing-points of dilute NaClAq, containing from c. 0.006 to c. 2.6 p.c. NaCl, *v.* Jones (Zeitsch. physikal. Chem. 11, 210). The freezing-point curves of mixtures of sodium chloride with calcium chloride and potassium chloride, *see* Lantsberry and Page (J. Soc. Chem. Ind. 1920, 39, 37; Chem. Soc. Abstr. 1920, ii. 250).

Solution of NaCl in water is accompanied by lowering of temperature and contraction; 36 parts NaCl in dissolving in 100 parts water at 12.6° lower the temperature to 10.1° (Rüdorff, Ber. 2, 68); Thomsen gives [NaCl, Aq]= −1180 (Thomsen's Thermochemische Untersuchungen, 3, 232). By mixing 36 parts NaCl with 100 parts snow, temperature falls to −21.3° (Rüdorff, Poggendorff's Annalen der Physik. und Chemie, 114, 79; 122, 337). NaCl is insol. absolute alcohol. Girardin (Annales de Chimie et de Physique, [4] 5, 146) gives the following data for S. in aqueous alcohol sp. gr. 0.9282; 10.9 at 4°, 11.1 at 10°, 11.43 at 13°, 11.9 at 23°, 12.3 at 32° 13.1 at 44°, 13.8 at 51°, 14.1 at 66°. Schiff (Liebig's Ann. Chem. 118, 365) gives S. in alcohol at 15° as follows: 28.33 in 10 p.c. alcohol, 13.25 in 40 p.c., 5.93 in 60 p.c., 12.2 in 80 p.c.

For the solubility of ethyl ether in solutions of sodium chloride, *see* Thorn (Chem. Soc. Trans.

1991, 2. 2). Solubility of mixtures of sodium and potassium chlorides in solutions of hydrochloric acid, *see* Hicks (J. Amer. Chem. Soc. 1915, 37, 844; Chem. Soc. Abstr., 1915, ii., 343).

For the contradictions between the real and calculated solubility of certain sodium salts, *see* Colson (Compt. rend. 1915, 161, 787; Chem. Soc. Abstr. 1916, ii. 84).

For the densities and specific volumes of sodium chloride solutions at 25°, *see* Hall (Washington Acad. Sci. J. 14, 167, April, 1924; Sci. Abstr. 1924, 27, 577). For the heat of dilution and specific heat of sodium chloride, *see* Richards and Rowe (Chem. Soc. Abstr. 1921, ii. 380). For the specific heat of aqueous solutions of sodium chloride, *see* W. R. and C. E. Bousfield (Chem. Soc. Abstr. 1919, ii. 134). For the vapour pressure of solutions of sodium chloride, *see* Speranski (Zeitsch. physikal. Chem. 1913, 84, 160; Chem. Soc. Abstr. 1913, ii. 923). For the relationship between the viscosity, density, and temperature of salt solutions, *see* W. J. Walker (Phil. Mag. 1914, [vi], 27, 288; Chem. Soc. Abstr. 1914, ii. 177.) The free energy of dilution of aqueous solutions, *see* A. J. Allmand and W. G. Pollack (Chem. Soc. Trans. 1919, 1020). For the pure preparation of sodium chloride, *see* Lohmann (Chem. Soc. Abstr. 1916, ii., 529; Shipper, Chem. Soc. Abstr. 1917, ii. 571).

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Sodium chlorite $\text{NaClO}_2 \cdot 3\text{H}_2\text{O}$, prepared from barium chlorite and sodium sulphate, forms lustrous laminae, and when anhydrous, explodes on percussion (Levi, Gazz. chim. ital. 1922, 52, i. 417; Atti R. Accad. Lincei, 1922, [v.], 31, i. 212; Chem. Soc. Abstr., 1922, ii. 567).

Sodium chromate Na_2CrO_4 . *See* Vol. II. p. 242.

Sodium dichromate $\text{Na}_2\text{Cr}_2\text{O}_7$. *See* Vol. II. p. 243. Solubility of sodium dichromate in alcohol, *see* Ranitzer (Zeitsch. angew. Chem. 1913, 26, 456; Chem. Soc. Abstr. 1913, ii. 965).

Sodium columbates.—The only sodium columbates which can be regarded as definite individuals are the salt, $7\text{Na}_2\text{O} \cdot 6\text{Cb}_2\text{O}_5 \cdot 31\text{H}_2\text{O}$, described by Bedford (Chem. Soc. Abstr. 1905, ii. 832), and the metacolumbate, $\text{Na}_2\text{O} \cdot \text{Cb}_2\text{O}_5 \cdot 7\text{H}_2\text{O}$, of Balke and Smith (Chem. Soc. Abstr. 1908, ii. 1044); Smith and van Haagen (J. Amer. Chem. Soc. 1915, 37, 1783; Chem. Soc. Abstr. 1915, ii. 692). *See* also Art. COLUMBIC ACID, Vol. II. 354.

Sodium cyanate NaOCN .

Sodium cyanide NaCN .

} For both these, *see*

under the head of CYANOGEN and CYANIDES, Vol. II. pp. 467 and 472. *See* also for sodium cyanide, Muetter (Chem. and Met. Eng. 1924, 30, 978; J. Soc. Chem. Ind. 1924, 43, B. 660.)

Sodium ferrate may be represented as $\text{Na}_2\text{O} \cdot \text{FeO}_3$, although it is not known in the pure condition. It is formed by oxidising iron or an iron compound in presence of an alkali either in the state of fusion, or in that of solution. The solution of the salt is characterised by its intense purple-red colour. It easily decomposes into oxygen and a ferrite (*see* Roscoe and Schorlemmer, Metals, 1201).

Sodium ferrite, say $\text{Na}_2\text{O} \cdot \text{Fe}_2\text{O}_3$. A compound formed by heating Na_2CO_3 with Fe_2O_3 the mixture loses CO_2 , and the dark green residue is sodium ferrite. It is scarcely decomposed by cold water, but at 70°–80° it is mostly decomposed, even if the solution of caustic soda pro-

duced is of sp.gr. 1.38. By the standing of a solution of sodium ferrate, say $\text{Na}_2\text{O} \cdot \text{FeO}_3$, crystals of sodium ferrite are obtained with evolution of oxygen. Sodium ferrite is also obtained by boiling ferric hydroxide with concentrated caustic soda. It has been used by many manufacturers for making sodium hydroxide solutions (*see* p. 229, col. 2, and p. 230, col. 2, par. 2); it occurs in the 'red bottoms' obtained in the last stages of the evaporation of caustic soda solutions in cast-iron pots.

Sodium ferrocyanide Na_4FeCy_6 . *See* under the head of FERROCYANIDES, Vol. II. p. 439.

Sodium fluorides NaF , $\text{NaF} \cdot \text{HF}$; and double fluorides.

Sodium fluoride NaF . *Sodium fluoride* occurs native in small quantities in nepheline syenite in the Los Islands, and in considerable amount as the double fluoride of aluminium and sodium, *cryolite* ($3\text{NaF} \cdot \text{AlF}_3$), found in Greenland. Sodium fluoride may be obtained from cryolite by treating the powdered mineral with an excess of strong caustic soda solution in iron pans, whereby the alumina is dissolved and sparingly soluble sodium fluoride remains behind. The pure salt is best made by neutralising a solution of hydrofluoric acid with sodium hydroxide or carbonate.

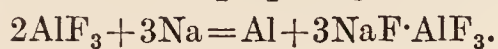
Sodium fluoride crystallises in very small colourless cubes of sp.gr. 2.766 (Schröder), which on heating melt at about 900°, but volatilise slightly at a lower temperature. The salt is only sparingly soluble in cold water (100 parts of water at 15° dissolve 4 parts NaF) and the solubility increases only slightly with the temperature. For the electrical conductivities of solutions of sodium fluoride of varying strengths, *see* Kohlrausch and Steinwehr (Sitz. der Berl. Akad. 1902, 581).

It is occasionally employed as an antiseptic and is used in lotions for certain affections of the skin; it has also been used for impregnating wood to prevent rotting, as by the Austrian Government Telegraph Dept. (J. Soc. Chem. Ind. 1918, 397, R).

Sodium hydrogen fluoride $\text{NaF} \cdot \text{HF}$ is obtained by dissolving NaF in hydrofluoric acid solution; it is much more soluble than the neutral salt, and can be obtained in crystals (rhombohedral) from a solution containing an excess of acid. Heated it evolves anhydrous hydrofluoric acid, hence it is used for the preparation of that acid and for mineral analysis. For the solubility of sodium fluoride in hydrofluoric acid, *see* Jehu and Hudleston (J. Chem. Soc. 1924, 125, 1451).

A great number of *sodium double fluorides* have been prepared as $2\text{Na}_3\text{PO}_4 \cdot \text{NaF} \cdot 19\text{H}_2\text{O}$, crystallising from Leblanc caustic soda liquors (Rammelsberg, J. pr. Chem. 1864 94, 237), but incorrectly analysed. In 1865 Baumgarten, (Zeit. f. Chem. N.S. 1, 605) found they contained fluorine and he believed also silica. In 1872 Thorpe (J. Chem. Soc. [2] 10, 660) again examined the crystals from soda liquors and proved them to have the above formula (*see* Baker, J. Chem. Soc. 1885, 47, 353). Many other sodium double fluorides are known as those described by Wagner (Ber. 19, 896); and $3\text{NaF} \cdot \text{AlF}_3$ *cryolite* used commercially for preparing sodium carbonate (*see* p. 178, col. 2, last two pars.), and sodium fluoride, and

aluminium, and also prepared artificially by Grabaus' method of preparing aluminium



Sodium halides, luminescence of, *see* Farnau (Chem. Soc. Abstr. 1913, ii. 743). Thermal analysis of sodium hydroxide and halides, *see* Scarpa (Atti R. Accad. Lincei, 1915, [v.] 24, i. 955; Chem. Soc. Abstr. 1915, ii. 633).

Sodium hydrazide, *see* Schlenk and Weichselfelder (Ber. 1915, 748, 669; Chem. Soc. Abstr. 1915, ii. 445). For the electrolysis of a solution of sodium hydrazide in anhydrous hydrazine, *see* Welsh (J. Amer. Chem. Soc. 1915, 37, 497; Chem. Soc. Abstr. 1915, ii. 256). For hydrazine sulphonate, *see* Traube and Vockerodt (Ber. 1914, 47, 938; Chem. Soc. Abstr. 1914, ii. 358).

Sodium hydrosulphite NaHSO_2 . This formula and name was given, 1869, by Schützenberger to a body first recognised by Schönbein, 1852. The correct formula was first given by Bernthsen, 1881, as $\text{Na}_2\text{S}_2\text{O}_4$, and the inaccuracy of the old name fully proved, since the substance contains no hydrogen. The old incorrect name is still used; the scientific name is sodium hyposulphite, *see* p. 232.

Sodium hydroxide NaOH , formerly called 'hydrate of soda,' *i.e.* $(\text{H}_2\text{O}, \text{Na}_2\text{O})$, commercially called 'caustic soda,' *i.e.* causticised soda, *i.e.* $(-\text{CO}_2 + \text{Na}_2\text{CO}_3)$.

To facilitate reference to particular details, *see* the following index:—

Historical, p. 211.

Anhydrous: Properties, p. 211; Commercial Forms, p. 212.

Hydrates and Solutions: Properties, p. 212; Commercial Forms, p. 213.

Uses, p. 213.

Industrial Preparation by—

(1) Leblanc Process, Recovery of the Caustic Soda initially existing in the Black Ash Liquor, in the form of Caustic Ash, p. 214; Red Liquor, p. 214; Cream Caustic and Anhydrous Caustic, p. 214.

(2) Causticising with slaked lime—

(a) Leblanc Black ash liquor, p. 215; Evaporation of the causticised liquor to sp. gr. 1.4–1.5, p. 217; to cream caustic or to fused caustic, p. 218; Detached, and Powdered caustic, p. 220; Losses and Analyses, p. 220; Close of the process, p. 220.

(b) Solvay ammonia soda ash and crude bicarbonate; Evaporation of the causticised liquor to 60°Tw., p. 220; to 105°Tw., p. 224; to 60 p.c. Na_2O solid and to fused caustic, p. 224.

(c) Lieber and Walzes sodium carbonate from nitre, p. 225.

(3) Electrolytic Methods: Introduction, p. 225; Special cells, p. 225; Anodes, p. 226; Evaporation and removal of salt, p. 226; Evaporation to powdered caustic, to the crystallisation of anhydrous caustic from molten monohydrate, p. 227.

(4) Methods of minor importance, chronologically arranged, and headed by the materials used in the final reaction, pp. 227–231.

Historical.—The action of lime on solutions of sodium carbonate (mineral alkali of the Egyptians, or the soda of plant ashes) has been known from very early times, and the caustic lye so produced has been used for soap-making.

The causticising was effected cold in presence of a little water, and the caustic lye was gradually washed out on a cloth filter; or more water was added, say six times the weight of the barilla (crude Na_2CO_3) (*see* p. 159, method 2), and half a part of quicklime and then boiled and settled. The clear liquors were used at once for the desired purpose. That the Egyptian mineral alkali was not a simple sodium carbonate but a more acid salt $(2\text{NaHCO}_3 \cdot \text{Na}_2\text{CO}_3 \cdot 2\text{H}_2\text{O})$ affected the above reaction to the extent of requiring lime to convert the complex carbonate into simple carbonate before the causticising began. The soda of plant ashes contained very variable amounts of real soda (Na_2CO_3), and hence the amount of lime required was also variable. The method of testing the lye to see if the reaction required more lime, was to add to a sample of the clear liquor a quantity of vinegar, which, by causing effervescence, indicated that the action was not complete.

The nature of this action was not understood till after 1752, when Black, of Glasgow, showed that mild alkalis differed from caustic alkalis by containing in combination a substance, 'fixed air' (carbonic acid gas), and that during the causticising this fixed air passed from the soda to the lime.

Berthollet discovered that the solution obtained may be purified by evaporating to the consistency of honey, adding an equal quantity of alcohol, and after settling pouring off the supernatant clear liquid from the bottom mass of crystals, partly evaporating the clear liquid, allowing it to stand, pouring off the clear liquid which is a solution of pure caustic soda in alcohol, and lastly evaporating in a silver vessel to obtain white crystals, that can be fused and volatilised, that powerfully attract water, and are extremely acrid and caustic (Nicholson's Dictionary, 1908). This pure substance was of considerable importance in analytical chemistry, and was known as 'caustic soda, pure by alcohol.'

The composition of caustic soda, at first supposed to be the pure alkali and a simple substance, was presumed by Lavoisier to be an oxide.

In 1807 Davy showed that by electrolysis it yielded a new body sodium, and oxygen, but he appears to have missed the hydrogen. Darcet in 1808, by alkalimetric tests on sodium carbonate and on caustic soda, showed that something was missing, and Berthollet, Gay-Lussac and Thenard, and Davy then made careful determination and showed that caustic soda was not the base formed by the combination of sodium and oxygen, but was the hydrate of that base, and accordingly was called 'hydrate of soda.' A table drawn up by Dalton, showing the percentage of anhydrous soda (Na_2O) in solutions of caustic soda, is given in Fownes' Chemistry, 1873, 331.

Anhydrous sodium hydroxide, properties.—At ordinary temperatures it is a colourless transparent crystalline body, having the form

of thick plates of apparently undetermined form. The least traces of iron or of manganese impart various colours—yellow, brown, green, blue. If noticeable quantities of NaCl or Na_2CO_3 are present the substance is white translucent to opaque and not noticeably crystalline.

The sp.gr. of NaOH is 2.130. When heated with a measured supply of heat it is found that at 299.6° there is a transition to another form, and 990 cal. per molecule are absorbed in the transition. On continuing the supply of heat the temperature then rises to 318.4° , when fusion commences and the latent heat of fusion per molecule is 1602 cal. (Hevesy, abstracted into J. Chem. Soc. 1910, Abst. 2, 835). The molten substance is colourless and transparent. Previous determinations, which are not many, have given lower results, probably owing to the presence of impurities.

The melted substance is exceedingly corrosive, and this action is increased by the presence of air or traces of moisture, which supply oxygen. If no oxidising agent is present then the NaOH itself at sufficiently high temperatures begins to be decomposed, for its hydrogen is in part evolved. Glass, porcelain, or fused silica vessels are rapidly dissolved; cast iron is generally used for the fusion but it is corroded more or less; silver is often used in the laboratory for the fusion but it is corroded; platinum also is affected; the best known substance for such fusions is pure gold. *See also* Wallace and Fleck, J. Chem. Soc. 1921, Trans. 1839. For the corrosion of glass by sodium hydroxide, *see* C. J. van Nieuwenburg (Chem. Weekblad, 1917, 14, 1034; Chem. Soc. Abstr. 1918, ii. 19). The corrosion of lead in sodium hydroxide solutions, *see* Henke and Smith (J. Phys. Chem. 1920, 24, 367; Chem. Soc. Abstr. 1920, ii. 526). The fusion of sodium hydroxide with some inorganic salts, *see* Boswell and Dickson (J. Amer. Chem. Soc. 1918, 40, 1773; Chem. Soc. Abstr. 1919, ii. 63). For the nature of the gas evolved when fused sodium hydroxide is dissolved in water, *see* Schramm (Chem. Zeit. 1919, 43, 69; Chem. Soc. Abstr. 1919, ii. 153).

It is remarkable that so hygroscopic a substance as NaOH can be crystallised anhydrous from its own solution, provided that the solution contains more than 74 p.c. NaOH (Pickering, and Griesheim Elektron) (*see* p. 227, col. 2, second par.).

The heat of formation from the elements is 101870 cal. For the solubility of sodium hydroxide in liquid ammonia, *see* Tchitchinaze (Chem. Soc. Abstr. 1916, ii. 431).

Anhydrous caustic soda, commercial forms.—It is mostly supplied in thin sheet-iron drums containing one solid lump of the material, generally weighing 6 cwts. This package is not readily handled by inexperienced hands. The best way to open a drum of caustic and break up the lump is as follows: Lay the drum on its side and strike the drum all over its cylindrical part with a sledge hammer. Insert a chisel under the rims and cut or force the ends off, then open the longitudinal seam and the whole package opens out flat, covered by a pile of broken pieces of caustic that can be conveniently removed with a shovel. It is advisable to wear goggles and thick cotton cloth gloves during these operations. The caustic must be

at once used, or else placed in vessels that can be closed practically airtight. It is also supplied in pieces of broken slabs, in flakes, in powder, and in small sticks, this last for laboratory purposes.

The impurities when made by the Leblanc process were many, Na_2CO_3 , Na_2SO_4 , NaCl , Na_2SiO_3 , $\text{Na}_2\text{Al}_2\text{O}_4$, Na_2S ; and $\text{Na}_2\text{O}\cdot\text{Fe}_2\text{O}_3$, Na_2MnO_4 , NaNO_3 , Na_3PO_4 , NaF , Na_3VO_4 , &c., in traces; when made from Solvay ammonia soda the impurities are very much smaller in amount; when made electrolytically from brine the impurities are still fewer and less in amount, and when the electrolysis is conducted with a mercury cathode the caustic is the purest made on the large scale, and is only exceeded in purity by the caustic made for laboratory purposes only, by treating sodium with water or steam.

For a simple method for the preparation of sodium hydroxide free from carbon dioxide, *see* Jacob Cornog (J. Amer. Chem. Soc. 1921, 43, 2573; Chem. Soc. Abstr. 1922, ii. 288). *See also* Kolthoff (Pharm. Weekblad, 1921, 58, 1413; Chem. Soc. Abstr. 1921, ii. 705).

Hydrates and solutions, properties.—At all temperatures below its melting-point NaOH eagerly absorbs water vapour, forming one or other of the following hydrates, or a liquid solution. For this reason the drums or other containing vessels should be closed air-tight. Dover and Marden (J. Soc. Chem. Ind. 1917, 995, Abst.) state that a column of NaOH 30 cm. long by 15 mm. diameter will so far dry a litre of air passing in about 30 minutes that P_2O_5 in a following tube will only absorb another 0.00016 gm. of moisture. Filhol (1847) stated that at atmospheric temperatures 100 parts of NaOH would absorb 552 parts of water. The efficiency of sodium hydroxide as a drying agent, *see also* Baxter and Starkweather (J. Amer. Chem. Soc. 1916, 38, 2038; Chem. Soc. Abstr. 1916, ii. 637).

The crystalline hydrates and their melting-points have been investigated by Pickering (J. Chem. Soc. 1893, Trans. 890), and to a less degree by others; they are—

$\text{NaOH} + \text{H}_2\text{O}$.	.	.	m.p.	64.3°
$3\text{NaOH} + 4\text{H}_2\text{O}$.	.	.	„	60.0
$2\text{NaOH} + 3\text{H}_2\text{O}$.	.	.		
$\text{NaOH} + 2\text{H}_2\text{O}$.	.	.	„	12.5
$\text{NaOH} + 3.11\text{H}_2\text{O}$.	.	.	„	2.7
$2\text{NaOH} + 7\text{H}_2\text{O}$.	.	.	„	15.5
$\text{NaOH} + 4\text{H}_2\text{O}$.	.	.	„	-1.7
$\text{NaOH} + 5\text{H}_2\text{O}$.	.	.	„	-12.2
$\text{NaOH} + 6\text{H}_2\text{O}$.	.	.		
$\text{NaOH} + 7\text{H}_2\text{O}$.	.	.	„	-23.5

Lunge's Alkali Manufacture states that the crystallisation of some of these hydrates has been used to purify impure solutions, and Lindroth (Bull. Soc. chim. Paris, [2] 17, 448) confirms this for $2\text{NaOH} + 7\text{H}_2\text{O}$.

$\text{NaOH} + \text{H}_2\text{O}$ is always deposited from solutions containing 51.7 to 74.0 p.c. NaOH . It forms large crystals of sp.gr. 1.829.

Solutions containing from 19.0 to 51.7 p.c. NaOH deposit one or more of the above higher hydrates.

Solutions containing less than 19.0 p.c. NaOH when strongly cooled do not deposit any hydrate but only ice.

Pickering (*see above*) showed that the freezing-points of caustic soda solutions form a series of curves lying on the following points:—

P.c. NaOH	5	10	15	20	25			
F.p. °C.	−4.4	−10	−17.9	−26.3	−16.2			
P.c. NaOH	30	35	40	45	50	55	60	
F.p. °C.	+1.0	12.2	15.5	7.5	11.8	34.0	52.6	
P.c. NaOH	65	70	75	80	85	90	95	100
F.p. °C.	62.2	65.0	70.2	137	205	247	284	318.4

but in the presence of certain crystalline hydrates the freezing-point may be decidedly lower. The last four figures are interpolated and approximate.

Freeth, in *Phil. Trans. Roy. Soc. Lond. A.* 223, pp. 35–87 (1922), has given data and figures for the solubilities at temperatures 0°–60° for caustic soda admixed with (1) Na_2CO_3 , (2) NaCl , (3) Na_2CO_3 and NaCl .

The heat of solution of NaOH in much water is +9780 cal. The specific gravities of solutions of NaOH 15°/4° have been determined by Pickering (*Phil. Mag.* [5] 37, 359–375), and are given in *Dammar's Anorg. Chem.* vol. ii. Pt. 2, 119. A table by Bousfield and Lowry (*Phil. Trans.* 1905, A, 204, 253) agrees with Pickering's figures up to 20 p.c. and then they are very slightly lower. Pickering's figures are—

P.c. NaOH	Units	Tens	Twenties	Thirties	Forties
0	0.99918	1.11107	1.22193	1.33121	1.43430
1	1.01061	1.12216	1.23306	1.34188	1.44416
2	1.02192	1.13325	1.24412	1.35247	1.45393
3	1.03311	1.14435	1.25513	1.36299	1.46362
4	1.04432	1.15545	1.26609	1.37345	1.47325
5	1.05546	1.16654	1.27706	1.38381	1.48285
6	1.06660	1.17762	1.28799	1.39409	1.49241
7	1.07773	1.18871	1.29888	1.40428	1.50193
8	1.08886	1.19978	1.30971	1.41436	1.51141
9	1.09997	1.21086	1.32050	1.42435	1.52087

A table showing the influence of temperature on the specific gravities of the solutions is found in *The Alkali-maker's Handbook*, Lunge and Hurter, 2nd ed. 143. The boiling-points of the solutions have been determined by Gerlach (*Zeitsch. anal. Chem.* 26, pp. 461–3, 1887), and the strength expressed as parts of NaOH per 100 parts of water.

B.p.	Strength	B.p.	Strength	B.p.	Strength
100	0.0	160	150.8	230	645.2
105	17.0	165	168.8	240	800.0
110	30.0	170	187.0	250	1000.0
115	41.0	175	208.3	260	1333.0
120	51.0	180	230.0	270	1739.0
125	60.1	185	254.5	280	2353.0
130	70.1	190	281.7	290	3571.0
135	81.1	195	312.3	300	6452.0
140	93.5	200	345.0	305	10526.0
145	106.5	210	425.5	310	22222.0
150	120.4	220	526.3	314	∞
155	134.5				

For volumetric determinations, *see* vol. i. 56.

The vapour tensions of NaOH solutions at 0° and at 100° are given in *Landolt Bornstein tables*; those at 100° are taken from *Tammann*

in *Mem. de l'Acad. Petersbourg* (7), 35, 1887; they are—

Grm. NaOH per 100 grm. Aq.—	1.75	2.09	7.79	12.18	14.34	22.40	23.27
Vap. tension mm.—	749.8	742.5	722.8	681.3	665.5	601.4	579.5
Grm. NaOH —	27.92	32.66	38.98	46.05	57.87	74.80	
Vap. tension—	553.7	511.2	453.7	396.2	307.6	217.0	

H. K. Moore, in *Met. and Chem. Eng.* 1918, 187, gives a small chart of the boiling-points from which the following figures are taken:—

P.c. NaOH	5	10	15	20	25	30	35
B.p. °C.	101	103	106	109	114	120	127
P.c. NaOH	.	40	45	50	55	60	62
B.p. °C.	.	134	143	152	162	174	179

Another set of determinations gave:

P.c. NaOH	5	10	20	30	40	50	60	70	80	
B.p.	—	102	105	110	115	126	140	160	180	210

At pressures less than atmospheric, caustic soda solutions of all strengths are boiled in many types of multiple effect evaporators, but the complete curves for strength—temperature—pressure have not been determined.

A small chart giving the heat units evolved or absorbed when NaOH solutions are diluted or evaporated is also given by Moore.

The solution is extremely corrosive on the skin, and though washing with water ultimately removes the caustic yet it also spreads it, and it is therefore much better to wash with a solution of 5–10 p.c. of magnesium sulphate, which effectually destroys the caustic (*see also* *Met. & Chem. Eng.* 19, 293).

For the heat of dilution and specific heat of sodium hydroxide solutions, *see* Richards and Rowe (*J. Amer. Chem. Soc.* 1921, 43, 770; *Chem. Soc. Abstr.* 1921, ii. 380). For the heat of neutralisation of sodium hydroxide, *see* Richards and Rowe (*J. Amer. Chem. Soc.* 1922, 44, 684; *Chem. Soc. Abstr.* 1922, ii. 425). For the heat of neutralization of sodium hydroxide with hydrochloric acid, *see* Keyes, Gillespie and Mitsukuri (*J. Amer. Chem. Soc.* 1922, 44, 707; *Chem. Soc. Abstr.* 1922, ii. 424).

A simple process for nitrating sodium hydroxide solutions, *see* Altmann (*Chem. Zeit.* 1913, 37, 1465; *Chem. Soc. Abstr.* 1914, ii. 70).

The action of sodium hydroxide solutions on cellulose, *see* *PAPER, MANUFACTURE OF*, Vol. V., p. 54, and Vol. IV., *MERCURISING*, p. 261. *See also* Leighton (*J. Phys. Chem.* 1916, 20, 32; *Chem. Soc. Abstr.* 1916, ii. 128).

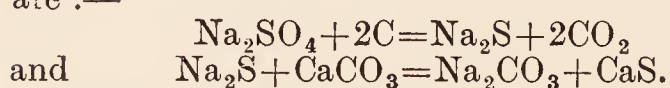
Hydrates and solutions, commercial forms.—The commercial forms of the hydrates are either solid blocks of 'cream caustic,' essentially mixtures of NaOH and $\text{NaOH}\cdot\text{H}_2\text{O}$ with varying degrees of purity, containing 60–70 p.c. NaOH ; or else 'caustic soda liquor' of 90° or 100°Tw., which are transported in iron drums with screw plugs, or else in iron tank wagons.

The uses of caustic soda are mostly for making ordinary soap (curd soap, soda soap); for isolating cellulose from many accompanying substances, as when making paper pulp from esparto grass, or when treating cotton hulls for the extraction of the cotton fibres; for cleansing and purifying cotton in all forms; for mercerising cotton;

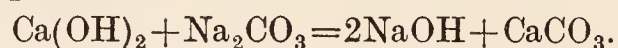
as a detergent for cleaning off old paint or grease; for converting sulphonates into phenols, as in the preparation of alizarin and resorcin; in the manufacture of formates, oxalates, and of indigo; for the manufacture of sodium; for the electrolytic preparation of oxygen and hydrogen. In the laboratory it is used as a standard of alkalinity; for absorbing CO_2 and other acid gases, using either a solution of caustic soda, or solid soda lime; for expelling ammonia, and for separating alumina from ferric oxide, &c.

The Methods of Industrial Preparation.

Leblanc process, recovery of caustic soda initially existing in the black-ash liquor.—The essential Leblanc reactions (founded 1787) are:—



A disturbing reaction attended by important consequences was $\text{C} + \text{CaCO}_3 = \text{CaO} + 2\text{CO}$, conditions favouring this secondary reaction were imperfect admixture of the ingredients, too intense local heating, and the general higher temperature occurring at the last stages of the main reaction. Thus it came about that the product always and unintentionally contained some CaO , and when lixiviated with water the CaO was converted into Ca(OH)_2 , which acted upon the sodium carbonate in accordance with the equation



Caustic ash.—The liquor from the black ash lixiviation was at first evaporated and ignited in one operation, and as the great bulk of the accompanying caustic soda was not carbonated by the furnace gases the soda ash produced always contained 10–24 p.c. of caustic soda. The furnace bed for this operation was either made of bricks or of cast-iron plates, both of which suffered excessive wear, and this was attributed to the caustic soda content; the early alkali makers were impressed with the idea that caustic soda was so extremely corrosive that nothing would withstand it (Davis, J. Soc. Chem. Ind. 1886, 351).

Red liquor.—The corrosion just mentioned and the possibility of fuel economy led to the evaporation of the black-ash liquor in iron tanks, and the constant or periodical removal by fishing or by draining of the crystals of $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ that were formed, and under these conditions the caustic soda accumulated in the mother-liquor, along with most of the other impurities. This was the first step towards the recovery of the caustic soda, but to the soda-ash maker it was only the means of converting the bulk of the product into a much purer form; from the mother-liquor he recovered the remainder of the alkali in a less pure form, by adding sawdust or coal slack and evaporating and igniting much as before. The details of all these methods are described under *Sodium carbonate* (see p. 171, col. 2, last par.).

Previous to 1852 there was a local sale of caustic soda solution in carboys and in very varying strengths, but generally of 70°Tw., but the cost and risk of the package, and the cost of cartage prevented the trade from developing into anything beyond a local one, as it could not compete with the low cost package of soda

ash and of quick lime, plus the small cost of local causticisation.

Evaporation of red liquor to cream caustic and to fused caustic.—The preparation of any form of solid caustic soda other than in the laboratory (see p. 212, col. 1, last par.) commenced in 1844 with Weissenfeld, who fused red liquors with nitre and obtained perfectly white solid caustic soda. There was no demand for the new article in commerce and the preparation was abandoned. In 1845 Geo. Brown, of Messrs. Tennants & Co., took out a patent for evaporating black-ash liquor till four-fifths of the soda salt had crystallised out, standing and draining, boiling down the mother-liquor till thick, adding a sufficiency of nitre and heating till all water was removed and the mass was in fusion.

Just before 1852 solid caustic soda was made at the Manchester Ardwick Bridge Chemical Works for Dr. Young's use in paraffin refining, by boiling down ordinary commercial caustic soda liquor of 70°Tw. in a pot 6 ft. diameter by 3 ft. deep until a sample would set on cooling, when the whole was baled into long iron trays, the solidified cake broken and packed in American potash barrels (Hart, J. Soc. Chem. Ind. 1886, 283; Davis, *ibid.* 351). In the same year solid caustic soda was sold in Philadelphia.

This process of solidifying caustic soda solutions was seen by Gossage, and combining this knowledge with the matter of Brown's patent, he saw the latent possibilities of solid caustic soda, and in May, 1853, took out a patent. This patent described the methods of purifying black-ash liquor (see under *Sodium carbonate*, p. 169, col. 2, last par.) by air, the evaporation of the clarified liquor till nearly all the sodium carbonate had been crystallised out (and with it certain impurities), and the concentration of the mother-liquor continued until a sample solidified completely on cooling.

The new product, known as Cream Caustic, aroused great attention in South Lancashire. Gamble was the first to adopt it on a really large scale; soap and paper makers used it readily, and other alkali makers of the district soon followed in the process, and later those on the Tyne. The solid was always coloured, the tints being blue, green, yellow, or red. The solid, a mixture of $\text{NaOH} \cdot \text{H}_2\text{O}$ and of NaOH , was not anhydrous, because the cast-iron evaporating pots would not stand sufficiently well the action of the caustic soda at the higher temperature required. It was customary to stop the evaporation as soon as the liquor approached 60 p.c. Na_2O .

In 1857 Gossage took out a further patent, and others also took out patents, among which was that of Bakewell for altering the method of packing already described, to pouring the hot liquor into thin sheet-iron drums so as to make when cold one large solid lump. This method of packing was a great improvement. The consumer sometimes dissolved the caustic out, but more generally used the method described, p. 212, col. 1, last par.

The method of treating the mother-liquor from the $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ crystals ('red liquor') was to boil it, while frequently fishing out the deposited salts, until it reached 70°Tw. and 121°C., whereupon it was cooled somewhat and the deposited crystals completely fished out. The

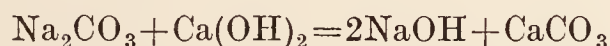
clean liquor was again heated, and to destroy the accompanying sulphides, sodium nitrate was added equal to about 11–15 p.c. on the finished product, and the boiling continued until the liquor reached 94°Tw. and 132°C., and again cooled a little and settled. The clear yellow liquid was run into a round cast iron pot and there again boiled. As the temperature rose the cyanogen compounds were decomposed with evolution of ammonia, and when a sample on cooling solidified properly the boiling was stopped, and the whole contents at once packed into a number of drums. Appropriating the water to the caustic soda, and omitting the minor impurities, cream caustic usually contained about

NaOH·H ₂ O	NaOH	Na ₂ CO ₃	Na ₂ SO ₄	NaCl
50·9	34·9	5·0	2·4	7·0

Causticising with slaked lime Leblanc black ash liquor.—In 1857, the demand for cream caustic exceeded the supply, and the Leblanc alkali makers, now relieved of their red liquor, began to causticise some of the black-ash liquor.

In 1858 Thomas patented the blowing of air by a steam injector into the liquor while under treatment with lime for the double purpose of keeping the lime mixed with the liquor, and of oxidising the accompanying sulphides to thiosulphate, and precipitating the ferrous sulphide which they held in solution. This method was most generally adopted, but it was gradually replaced by mechanical agitation, which necessitated a subsequent special treatment to remove the sulphides.

The reaction



is not a simple one for the following reasons:—

(1) Some sodium carbonate always remains unacted upon, and the amount of this portion increases considerably with the strength of the sodium hydrate solution produced. The reaction is reversible within certain limits.

(2) Some sodium carbonate is lost from the solution, and is found again in the insoluble calcium carbonate precipitate produced by the main reaction. The amount of this loss is about 2·5–3·0 p.c. The cause of the loss is that double sodium calcium carbonates are formed, that are only very slightly soluble in water: Na₂CO₃·CaCO₃·2H₂O under the usual conditions, Na₂CO₃·CaCO₃·5H₂O below 40° (Gaylussite), and Na₂CO₃·CaCO₃ if the sodium carbonate solution is very strong.

(3) The speed of the reaction is not great, and is largely dependent upon the temperature. At ordinary temperatures the reaction is not complete in several days; at 62° more than 40 hours are required; at 108° the reaction is finished in 2½ hours. The completeness or incompleteness of the reaction is not influenced by the temperature, only the speed of the reaction.

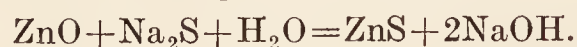
For reasons (1) and (2) it is advisable to work with weak solutions, but the advantages thus obtained are counterbalanced by the increased cost of evaporating the extra solution, and the advantage of working with strong solutions is counterbalanced by the costs in labour and material of the Na₂CO₃·H₂O to be fished out during the evaporation.

The best strength of liquor to causticise has therefore varied; it was 16–20°Tw., but has been as low as 14°, it rose to 22°, and is now 20°–26°Tw., and at these strengths the amount of sodium carbonate escaping conversion is 8–9 p.c.

Many investigations have in more recent years been made into the lime causticising operation, and several processes have been suggested with the object of increasing the proportion of causticised to uncausticised soda, *i.e.* of NaOH to Na₂CO₃ in the final liquor when working at higher strengths of solution. Patents were taken out by Parnell (4144, 1877, and 2203, 1878), by Wells (3803, 1879), by Menzies (3804, 1879), and by Herberts (3577, 1882) for conducting the causticising operation under pressure, which was claimed to give increased causticity per cent. at strengths up to 1·2 sp.gr. The Parnell process was tried extensively on a large scale and failed. The investigations of Lunge and Schmidt (Ber. 1885, 3286) showed that working under increased pressure did not affect the percentage of causticity obtained. Herberts, in a later patent (D. R. P. 43492), claimed that higher causticity could be obtained with liquors of 1·14–1·16 sp.gr. when working under diminished pressure. Later investigations are those of Bodländer (Zeitsch. angew. Chem. 1904, 1519), Leblanc and Novotny (Zeitsch. anorg. Chem. 11, 181), Wegscheider and Walter (Chem. Zentr. 1907, i. 1015; and Monatsh. 26, 684; 27, 13).

Purification of the black-ash liquor, before or after causticising.—An important point is the removal of the sulphide always present in Leblanc liquors. There has been much discussion as to the best way of doing this, and many expedients have been tried. Hargreaves proposed oxidation of the heated liquor by blowing air through it; the oxidation was very slow and incomplete. Pauli advocated the addition of a small quantity of 'Weldon mud' (*see art. CHLORINE*, under heading *Weldon bleaching-powder process*) (Eng. Pats. 1306 and 1530, 1879) to the caustic liquor while it was being blown with air. A detailed description of these oxidising processes has been given by Jurisch (Dingl. poly. J. 240, 55). The removal of the sulphide by electrolysis was patented by Merle in 1875, and tried at Salindres; it was the subject of a later patent by Deacon, Hurter and Elmore (Eng. Pat. 800, 1885). Chance (Eng. Pat. 5920, 1885) decomposed the sulphides by a mixture of ferric and calcium hydroxides or carbonate, produced by precipitating ferric chloride with a large excess of lime or calcium carbonate. Some further particulars of these processes will be found under the head of *Sodium carbonate Leblanc process* (pp. 169 to 170).

The later practically universal practice is to remove the sulphide by the addition of zinc oxide to the causticiser, or by the addition of sodium nitrate to the finishing pots, or both methods are employed successively. The zinc oxide acts according to the equation:



The zinc oxide solution may be obtained by dissolving metallic zinc, or crude zinc oxide in hot caustic soda liquor of about 1·13 sp.gr., and the solution so obtained is run into the causticiser during the causticising process.

Causticising plant and process.—The appa-

ratus used is usually a large wrought-iron vessel, fitted with either horizontal or vertical mechanical agitators and a basket (see *b* in Figs. 40 and 41), into which the lime required is placed.

The operation is usually carried out as follows: Well-settled vat liquor is heated as far as possible by waste heat or exhaust steam, and run into the causticiser where it is diluted to a strength 1.1–1.13 sp.gr. with weak liquor obtained from a later stage of the causticising process, and by water, both of which should also be preheated when possible by waste heat. The

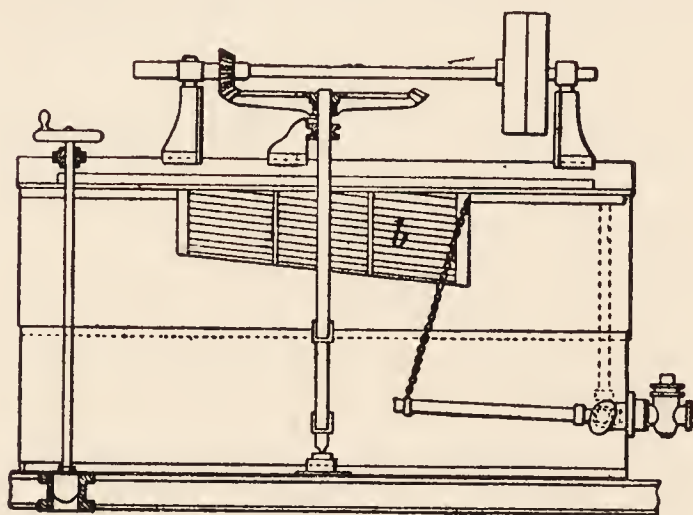


FIG. 40.

quantity of total liquor in the causticiser should be sufficient to just cover the bottom of the cage *b*. The liquor is heated to boiling by steam through a steam pipe not shown in the figures, and the steam being now shut off large lumps of quicklime are gradually and carefully placed in the cage so as to prevent splashing and to prevent the adjacent liquid from boiling over, the heat of hydration supplying heat to make good losses by radiation. More vat liquor and weak

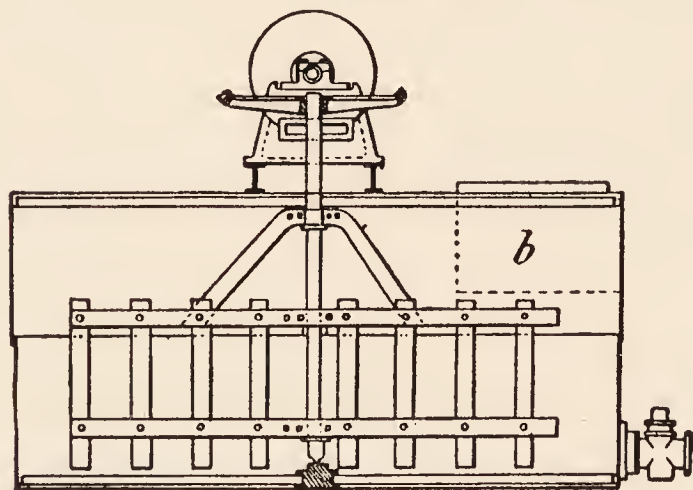


FIG. 41.

liquor are gradually run in and the lime added until the causticiser is full and the calculated quantity of lime added. A filtered sample is tested to find the caustic soda and the soda existing as carbonate, and if the soda as caustic does not exceed 90 p.c. of the total soda more lime is added.

The agitator is stopped and the muddy liquor allowed to settle for about 1½ hours. The comparatively clear liquor is very carefully run off the top by the swivel pipe shown in Fig. 40 (but it will not require lowering so much as shown in the figure) and run to settlers. The causticiser remains, perhaps, one-third full of caustic liquor and lime mud that cannot be further separated by settling. This can either (1) be

run out direct on to a filter bed; or (2) the mud being left in the causticiser, the causticiser can be filled up with water, agitated and again settled; the weak liquor so obtained (together with subsequent washings from the filter) is used for diluting another batch of vat liquor, as already alluded to, and the washed mud is run on to a filter bed and again washed with water; or (3) the mud being left in the causticiser, one or two more batches are causticised without running off the lime mud. This saves time and makes it possible to work all batches but the last with a larger proportion of excess free lime than would be economical for the single batch. The increased quantity of free CaO slightly increases the causticity per cent. obtainable.

Washing and using the lime mud.—When the lime mud is to be emptied, the mud is made fluid by working the agitator or by using hand rakes. The valve shown on the left hand of Fig. 40 is opened and the mud run by a 3 or 4 in. pipe, not shown in the figure, into the filter.

The filters vary considerably in design and arrangement; Fig. 42, however, is representative

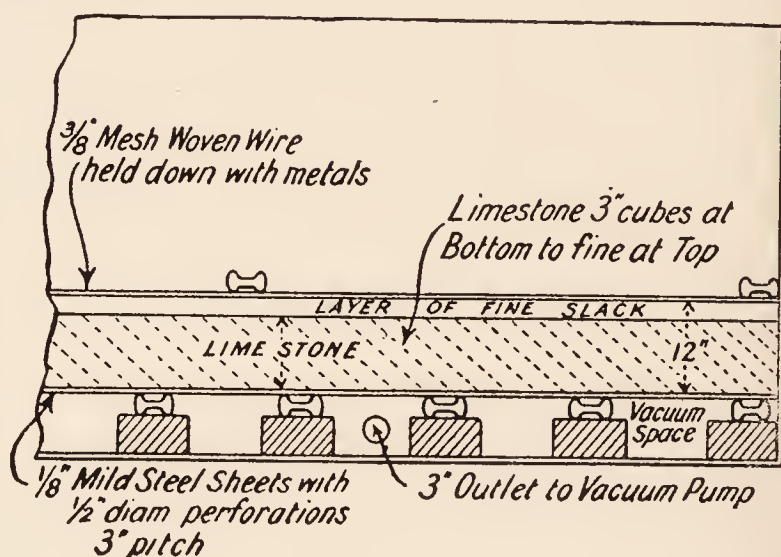


FIG. 42.

of a large number of filters, and shows a thoroughly efficient and satisfactory apparatus.

As soon as the filter bed is covered with liquid mud the vacuum pump is started, which both removes the filtrate and the air from under the bed. As soon as the surface of the mud begins to dry, cracks are likely to appear. These require raking over or patting with a spade to close them up. Hot water is run on to the mud to wash out the caustic liquor which it contains. Finally, the vacuum pump is kept going for some time to suck the mud as dry as possible, but under the best circumstances it retains over 40 p.c., and usually nearly 50 p.c. of water. With careless washing, with cracks in the bed of lime or round the sides of the filter, or holes and inequalities in the filter bed, there may be a loss of soda amounting to 4–6 p.c. on the weight of the lime mud, and as there are about 2 tons of lime mud to the ton of Leblanc 70 p.c. caustic soda, it is evident that this may be a very serious matter. With good washing the loss may be reduced well below 1 p.c. on the lime mud.

Other forms of filter for caustic lime mud have been suggested of a more or less mechanical nature, but have not met with extended use, see patents by J. Brock and T. Martin, 2127, 1887; G. H. Bolton and T. A. Bullough, 14563, 1888; Hurter and Driffeld; Solvay

(Eng. Pat. 4725, 1896); and Houghton and the United Alkali Co. (Eng. Pats. 7957 and 28791, 1903).

For reference to recent American patents, see later the account *Caustic soda from ammonia soda* (p. 220, col. 2, par. 3).

The following analyses of caustic lime mud are given by Davis (Chem. News, 32, 187):—

CaCO_3	.	.	.	40.2	42.0
Ca(OH)_2	.	.	.	3.7	3.1
SiO_2	.	.	.	0.7	0.8
Al_2O_3	.	.	.	0.2	0.3
Fe_2O_3	.	.	.	—	0.7
MgO	.	.	.	0.1	0.1
Na_2O	.	.	.	1.8	1.6
H_2O	.	.	.	48.0	46.6
				99.6	99.6

Lime mud was frequently employed to replace part of the limestone required for the revolver

charge in Leblanc's sodium carbonate process (see pp. 165 to 167). For this purpose it was used in the wet condition. In this way the soda contained in the mud was probably recovered, and some limestone was saved, but there were counterbalancing fuel costs.

In some works the attempt has been made to convert the calcium carbonate in the mud to quicklime, and it is reported that this has been economically done in the rotary kilns used in the manufacture of Portland cement.

The lime mud is also used as a raw material for the manufacture of Portland cement (Rigby, J. Soc. Chem. Ind. 1888, 301).

A very important and increasing outlet for caustic lime mud is for liming the soil. For correcting acidity in the soil calcium carbonate is as useful as the oxide, and the finely-divided condition of caustic lime mud renders it particularly suitable. The lime improves the soil by defloculating the clay masses. In a small degree it is a plant food, but in much larger

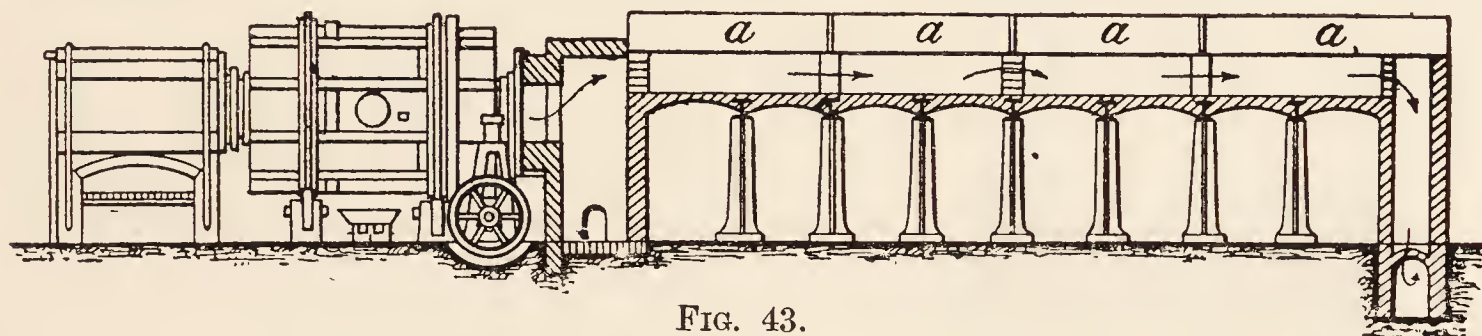


FIG. 43.

measure it helps to bring into action the insoluble reserves of nitrogen and potassium in the soil. It is the best remedy for the finger-and-toe disease in turnips and swedes. See leaflet No. 170 of the Board of Agriculture and Fisheries.

Evaporation of causticised black-ash liquor to sp.gr. 1.4–1.5.—The liquor from the causticisers contains 9–10 tons of water per ton of 70 p.c. caustic soda, and the economical evaporation of this large quantity of water has always been one of the technical problems of caustic soda manufacture.

The methods used by Leblanc soda ash makers were at once known to be quite inapplicable, because (1) during the whole processes of evaporation the caustic soda does not crystallise out (like $\text{Na}_2\text{CO}_3\cdot\text{H}_2\text{O}$), but remains liquid; (2) strong solutions of caustic soda are intensely destructive on all brickwork, and are far more corrosive on wrought iron or cast iron than is sodium carbonate at any stage of its evaporation and roasting; (3) while sodium carbonate solution at a boiling heat is hardly if at all acted on by the carbon dioxide of flue gases, caustic soda solution rapidly absorbs carbon dioxide, hence the economical but rather dirty top-heated pans for soda ash could not be used and less economical but cleaner bottom-heated pans had to be employed.

The usual custom was to do the first part of this evaporation by means of the waste heat of the black-ash furnaces, which in those times were almost entirely hand-worked furnaces.

Fig. 43 represents a revolver fitted with shallow wrought-iron bottom-heated pans *a, a, a, a*, to utilise the waste heat by concentrating the weak caustic soda solution obtained from the causticisers.

The causticised liquor from the settlers is fed in a steady stream into the pan furthest from the revolver from which it overflows from pan to pan, until it leaves the front pan at 1.2 sp.gr.

The next process, called 'concentration,' carries the liquor up to such a strength that the bulk of the Na_2CO_3 left in the causticised liquor and the Na_2SO_4 from the vat liquor separate out, forming 'caustic salts.' A vessel frequently used in former days, is the boat

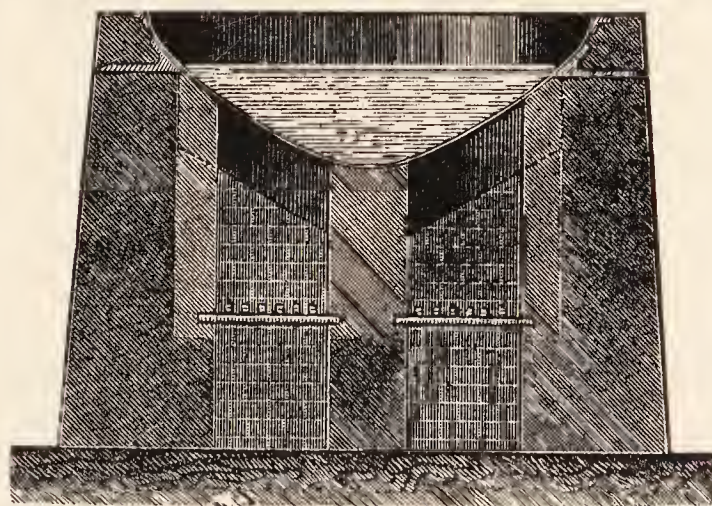


FIG. 44.

pan, of which Fig. 44 is a cross section. It is made of cast iron $1\frac{1}{2}$ – $1\frac{3}{4}$ ins. thick, and its dimensions are about 12 ft. long, 8 ft. wide, 3 ft. 6 ins. deep, and, owing to its narrowness and shallowness, the salts may be fished out as soon as they begin to settle out in the quiescent portion of the liquor just over the central wall which is built wide for this purpose. The deep fireplace and the long following shallow horizontal flue are shown in the figure.

The more recent form of concentrators is

large cast-iron self-fired vessels called caustic pots (see Fig. 45). These vessels are made of cast iron specially selected for the purpose, and vary in size in different works. A common size is 10 ft. diameter by 6 ft. deep. The setting of the caustic pot is a matter of importance, as the life of the pot is largely dependent on the prevention of contact between a flame blast from the grate and the metal of the pot. It is usual, therefore, to protect the pot opposite the fireplace with a guard wall, partly shown in the figure as an arch.

The pot is filled with liquor, the fire lit, and the loss by evaporation is made up by a constant slow stream of fresh liquor until the sp.gr. has risen to 1.4–1.5, depending on the purity and consequent strength of the caustic it is intended to pack. The fire is then drawn and the pot allowed to settle for some hours.

After settling the clear liquor is baled out with a large wrought-iron ladle cleverly balanced on the pot edge and worked with little exertion by an experienced man, either into an adjacent pot for the finishing operation if the purity required is low, or into a tank from which it is pumped to settlers, where a further

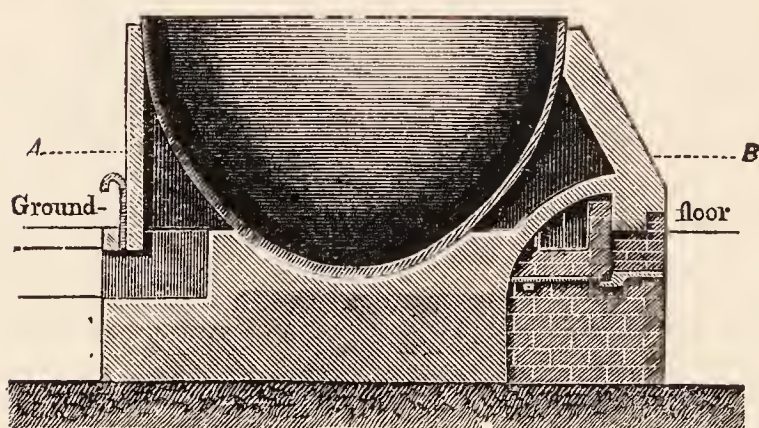


FIG. 45.

batch of salts settles out on standing and cooling, if the purity required is high.

When the clear liquor has been taken out of the pot, the salts are fished out with a perforated ladle and are drained on a drainer or in a centrifugal machine. The salts are a great source of trouble and expense, as per ton of caustic obtained (70 p.c. Na_2O purity) their amount is 5–7 cwts. Their composition averages:

Na_2CO_3	Na_2SO_4	NaOH	H_2O , etc.
39	20	9	32

The greater part of the salts is dissolved and mixed with the liquors feeding the causticiser and recausticised to recover the Na_2CO_3 and the NaOH ; but a small part is returned to the black-ash revolver to keep down the accumulating Na_2SO_4 .

In 1859 Dale patented the first concentration of the causticised liquors in steam boilers so that the steam could be utilised, and it was mostly utilised for heating the causticisation tank. The liquor was concentrated in Lancashire boilers to something like $30^\circ\text{--}40^\circ\text{Tw.}$, but in all cases so low that there was no danger of depositing sodium carbonate or other salts. But the boiler was even at these strengths attacked, not by the caustic soda but by reason of the accompanying sulphide, which therefore had first to be removed by blowing

with air or by precipitation with lead oxide. The method was never in general use, but in some factories was used for many years. After a few years the boiler repairs become very heavy, the rivet heads sheared, and the joints leaked.

Another form of concentrator is the multiple effect evaporator, but as this apparatus was introduced into alkali works by the Ammonia Soda Works it will be described under the head of *Caustic soda from ammonia soda ash* (see p. 221, col. 1, Evaporation, to p. 224), merely mentioning that the incrustations on the evaporating tubes is much more troublesome with Leblanc caustic liquors, and the stoppage of the evaporator for cleaning the evaporating tubes deterred many Leblanc alkali makers from adopting it.

Evaporation of caustic liquor of 1.4–1.5 sp.gr. at 15°C. into either cream caustic or into fused caustic.—The evaporation to cream caustic is essentially the same as the evaporation of red liquor to cream caustic described, p. 214.

The following is an analysis of cream caustic from black-ash liquor:—

$\text{NaOH}\cdot\text{H}_2\text{O}$	NaOH	Na_2CO_3	Na_2SO_4
39.6	47.3	1.4	2.2
NaCl	Na_2SiO_3	Na_3AlO_3	Na_2SO_3
7.8	0.2	1.3	0.1

This product (like that made from Leblanc red liquor) was never white.

The complete evaporation to fused caustic originated in 1844 and 1845, when Weissenfeld and Brown (see p. 214, col. 2, first par., to p. 215) obtained anhydrous caustic soda, but their processes were abandoned. In 1857 Deacon, and in 1859 MacBryde, had also made a white anhydrous caustic soda. In 1860 Ralston (put forward as a patentee by MacBryde) described the manufacture of *white* caustic soda by continuing the boiling after the strength of cream caustic had been obtained, and simultaneously raising the temperature until the iron colouring the contents of the pot sinks to the bottom of the pot, and the clear molten caustic soda rests above it, and instead of destroying the sulphide impurities by adding large quantities of sodium nitrate (as described by Weissenfeld in 1844, and as practised more and more generally from 1853 by those using Gossage's patents), the sulphides were removed in a new way by blowing quantities of air through the anhydrous molten caustic soda.

In 1862 white caustic soda was exhibited by Deacon in London and by Pauli in Manchester, and June 28 Pauli published his process in use at St. Helen's in the Chem. News, where it was also described by Norman Tate.

The new process was quickly adopted in the Lancashire alkali works, and in 1870 it extended to the works on the Tyne and in Glasgow, and displaced the method used in a few alkali works of converting black-ash liquor into soda ash, and then causticising it.

Some of the main working methods for the evaporation of the caustic soda solution are next described.

The apparatus used is one or more cast iron caustic pots similar to those described above (Fig. 45) for the concentration.

If one pot is worked by itself it is continuously fed with the liquor, and when, after con-

siderable evaporation, the flowing of this solution on to highly-heated, nearly anhydrous caustic causes so much spluttering as to become dangerous, it is usual either to sprinkle the liquor over the surface of the pot by running it through a perforated plate or ladle, or else to cover the pot with the loose wrought-iron lid which is, in any case, used as a cover during the last stage of the finishing. When the pot is full of a quietly fused mass the above-mentioned loose lid is put on and the pot gradually heated still further till the rusty red colour of the mass vanishes and the liquor becomes clear and practically colourless.

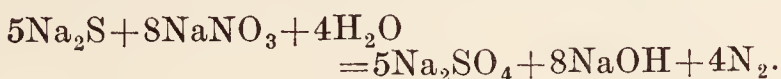
If two pots are worked together, the above-named dangerous feeding is avoided, and hence this is the more general way of working. The liquor is fed simultaneously into two adjacent pots, and the boiling started; the boiling is brisk, and this continues with slow feeding of more liquor into each until both pots reach a peculiar foamy condition well known to the workmen, and are apparently full. The liquor feed to both pots is stopped, and also the fire on one of the pots. The liquor in the standing pot is then baled as required into the boiling pot until the working pot is full, to within say four inches of the top, of almost anhydrous caustic soda in a state of quiet fusion, clear and essentially colourless, and the standing pot is empty. To confine the biting spray evolved during the final stage, the pot is covered and the feeding effected by a long shute passed through a small hole for feeding and inspection.

As caustic soda is sold at definite strengths, 60, 70, or 76 p.c. Na_2O , &c., it is necessary to test how near the contents of the pot are to the required test. A sample is taken out by a small ladle and poured on to a spade or into a mould, allowed to set, and then bottled for testing in the laboratory. The caustic in the pot is usually found too high in test, and has to be reduced by the addition of a calculated and weighed quantity of well-dried salt (NaCl). The salt is added in small quantities through the hole in the sheet-iron cover. The salt decrepitates badly when it comes in contact with the caustic soda, and causes considerable irritation to those near the pot by spreading finely-divided caustic spray through every outlet in the pot cover. After addition of the salt the fire has to be again urged, as the fusion of the salt cools the caustic soda considerably, and unless reheated it will not settle satisfactorily, and the solid caustic soda would be tinged reddish from the suspended ferric oxide hydrated.

The molten caustic may still contain sulphides even if the bulk of these was removed by blowing the black-ash liquor with air while causticising, or by adding zinc oxide while causticising, or by blowing air through the molten caustic; it may also contain ferrocyanide even though much of this may have been removed by adding zinc oxide while causticising, or if the temperature has already decomposed the ferrocyanide into cyanide then cyanide and also thiocyanate may be present; all these objectionable impurities are removed by the next process of adding nitre.

It is important not to add the sodium nitrate until the pot temperature has become high, say

between 420° and 470° , because if it is added before the pot is sufficiently heated, the caustic liquor has a great tendency to boil over. The sodium nitrate is added until a small sample of caustic taken from the pot is only slightly blackened by a solution of lead acetate. The reaction with the sulphides is probably:



When the whole of the sulphide is removed sodium manganate is formed in the caustic soda and colours the finished product green. If accidentally the limit is passed and on sampling a blue or green colour is observed in the solidified sample, it can be rectified by the addition of a small quantity of finely-divided sulphur to the fused mass in the pot.

The last substance to be removed is the ferric oxide. This does not settle readily unless it has been fully dehydrated by urging the fire until the product acquires a just visible dull red colour in the shade of its cover, when the fire is at once drawn and the pot allowed to settle and cool. The settling takes from 6 to 12 hours, and during this period the impurities, which consist chiefly of ferric oxide, alumina, and silica, form a rather heavy mud on the bottom of the pot.

The clear settled caustic is, after cooling to about 325° , ready for packing; this is recognised by the ease with which samples set and often by a deposit of solid caustic around the edges of the pot; packing is at once commenced and continued without interruption.

By far the greater proportion of the caustic soda is packed in what are called caustic drums. The packing consists in ladling the molten caustic into the drums. It is usual to surround one side of the pot to be packed with a semicircular row of drums into which the caustic is successively conveyed by a wrought-iron shute, the lower end of which is moved from drum to drum.

The drums are cylindrical sheet-iron packages (see Fig. 46) with lap joints. The sheets are neither riveted nor welded, but are folded over each other and rolled under pressure; they are a cheap package.

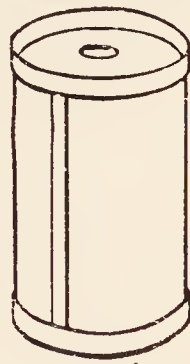


FIG. 46.

No leakage occurs if the caustic was only just above its melting-point, as already described, and if the drums are partly filled in rotation and the complete filling finished afterwards. When the baling begins to disturb the bottom sediment the work has to be done very carefully, and when no more sufficiently clear product can be obtained baling into drums is stopped. From the fact that the caustic is a solid block, caustic in drums stows well for transit.

Caustic bottoms.—The residue in the pot, called 'caustic bottoms,' is a mixture of caustic soda, with the impurities settled out as above described, is well stirred and the deep red muddy liquor is baled similarly into drums for sale at a reduced price as 'caustic bottoms,' or else into iron barrows for solution, settling and returning the well settled liquor to the process.

The following is an analysis of caustic

bottoms taken from a pot that had packed 70 p.c. caustic:—

NaOH	p.c.
Na ₂ CO ₃	63·2
Na ₂ SO ₄	1·6
NaCl	2·0
Na ₂ S	5·4
Na ₂ SiO ₃	0·1
Na ₆ Al ₂ O ₆	2·4
Fe ₂ O ₃	14·2
					10·9
					99·8

but they vary in strength between 53 and 63 p.c. Na₂O. For many purposes the solution of 'caustic bottoms' after well settling is as efficient per unit of free Na₂O as that made from white caustic itself.

Detached caustic soda is made for the convenience of small users, usually by baling a thin layer of the molten caustic on to heavy iron plates, where it almost immediately solidifies, without attaching itself to the plates and is then easily broken into pieces which are packed in casks. An apparatus to do this work was invented by Boulouvard (D. R. P. 34040). A more recent apparatus (1920) is that of Minton and the United Alkali Co. Pat. 141942. A circular revolving table has the molten caustic poured on to it from one fixed position, and is kept cool by cast webs under it which dip into water; after travelling nearly three quarters of the way round it passes under a radial ridged or toothed roller which breaks the caustic into pieces, that are next swept off the table by a radial steel wire cylindrical brush and an endless chain conveyor.

Powdered caustic soda.—Menzies (Eng. Pat. 4274, 1879) and Harned (Eng. Pat. 4677, 1883) described apparatus for grinding to a powder and sieving. Caustic soda powder is produced to some extent for the market.

Losses of soda in the Leblanc process.—Of the total Na₂O charged into the revolver as salt-cake the average production in the form of finished caustic soda is about 85 p.c.

The greater part of the 15 p.c. loss is carried away in the black-ash waste, partly as soluble soda through imperfect washing of the black-ash waste in the lixiviating vats, and partly as insoluble compounds with the alumina and silica derived from the ash of the mixing fuel, the revolver lining, and the limestone; part is lost as soluble soda and as insoluble soda in the lime sludge from causticising; part is lost in the rejected salts fished out during evaporation, and part as insoluble soda in the caustic bottoms.

Analyses.—The commercial methods of analysis of caustic soda are given in Lunge's Technical Chemists' Handbook, p. 184.

The following are some analyses by Huson and Hardwick of Leblanc commercial caustic soda of different strengths:—

	60 p.c.	70 p.c.	76 p.c.	77-78 p.c.
NaOH	79·8	86·6	95·4	96·92
Na ₂ CO ₃	1·1	2·7	2·0	1·45
NaCl	15·1	6·9	1·5	0·58
Na ₂ SO ₄	3·6	3·2	1·1	0·73
Na ₂ SiO ₃	0·1	0·5	0·2	0·32
Fe ₂ O ₃ , Al ₂ O ₃ , and CaO	0·4	trace	0·2	trace
Insoluble	—	0·2	—	—
	100·1	100·1	100·3	100·0

In the cases of the first two analyses it must be remembered that the NaCl is mostly added to adjust the strength to the guaranteed test.

The close of the Leblanc process.—The Leblanc processes for the manufacture of caustic soda, though competing keenly with the manufacture from Solvay's ammonia soda, were still flourishing in 1914, but during the war there were large extensions in the electrolytic manufacture of caustic soda, and by 1921 the Leblanc process, because of its large fuel and labour costs, was no longer used except where one of its by-products keeps the combined manufacture remunerative, and the United Alkali Company have now adopted the electrolytic manufacture of caustic soda by the Gibb's diaphragm process (Clayton, J. Soc. Chem. Ind. 1921, 443, R).

Caustic soda from Solvay ammonia soda ash by slaked lime.—Another source of sodium carbonate for the manufacture of caustic soda is from Solvay's ammonia soda process, the initial product of which is sodium bicarbonate, and the details of this process will be found under *Sodium bicarbonate* (see p. 182, col. 1, to p. 193), and the second process is the conversion of the bicarbonate into sodium carbonate, and the details of this process will be found under *Sodium carbonate* (see p. 176, method 12, to p. 178). These processes were made successful in 1863, and they have increased in output ever since.

The impurities in 'ammonia soda ash' are very much fewer and very much smaller in amount than in Leblanc red liquor, or in Leblanc black-ash liquor, or in Leblanc soda ash, and hence many of the difficulties connected with those processes do not exist when making caustic soda from ammonia soda ash. The impurities, say 1·20 p.c. NaCl, 0·12 p.c. Na₂SO₄, and 0·40 p.c. of CaCO₃, MgCO₃, and Fe₂O₃, do not call for any special treatment.

The details required for successful causticising have already been described under causticising of Leblanc black-ash liquors (see p. 215, col. 2, last pars., to p. 217), and the apparatus there figured (Figs. 40 and 41) are also applicable for dissolving ammonia soda ash and for causticising the solution so obtained.

In this way paper makers, textile bleachers, and soap makers, who require a solution of comparatively low strength caustic soda liquor, prepare their own caustic liquor. When actual costs are obtained, however, it is very rarely found that the production of their own caustic liquor pays when compared with the price of already made caustic. Local conditions as to prices of fuel, lime, and facilities for waste deposit vary too much to enable a standard comparison to be made, applicable to every case, but it is necessary to remember that to produce caustic liquor of 1·1-1·13 sp.gr., equivalent to 1 ton 70 p.c. caustic soda, requires from actual results in such works, 29-30 cwts. 58 p.c. soda ash, 17-18 cwts. lime, 20 cwts. fuel. In addition to this there have to be deposited 2½-2½ tons of caustic lime mud, and the wages, repair and capital charges to be met. The soda liquor obtained in this way contains about 90 p.c. of its total soda only as hydroxide, the remainder as carbonate, and if great care is not exercised in the washing of the lime mud on the filters before sending to the tip, the soda losses may be largely increased.

Caustic soda from Solvay crude bicarbonate.—In the ammonia soda works it is not necessary to use the finished soda ash, the moist washed sodium bicarbonate is agitated while steam is blown in, and the exit steam carries with it not only the carbon dioxide evolved by the decomposing bicarbonate, but also the small quantity of ammonium carbonate left in the washed bicarbonate, and both these volatile constituents are collected and utilised. When about 75–80 p.c. of the alkali is converted into normal carbonate the steaming is stopped, the paste dissolved in water, and causticised with lime as before described, but an extra amount of lime has to be added because of the 25–20 p.c. of bicarbonate still present, and this causes a rather larger loss than usual in the form of sodium-calcium carbonate. These troubles caused the trial of another process, which see above under the head of *Sodium carbonate*, causticised by heating with ferric oxide (p. 230, col. 2, *Ferrite*).

A more recent plant is the continuous apparatus devised by American workers (see *Met. & Chem. Eng.* 1915, 13, 514; 17, 599; 18, 169 and 376; abstracted *J. Soc. Chem. Ind.* 1918, 28, A). The first article gives a description and figures of the continuous thickener and the agitator, and also a general schematic plan of the whole plant. The last article describes the continuous working of a plant producing 50 tons NaOH per day, in which the liquor produced contained 9.4 p.c. NaOH, and the lime mud was so completely washed that the loss of soda was only 0.25 p.c., and the cost of labour and power was only two shillings per ton of caustic produced. The causticising is effected in a series of three Dorr agitators, whence it flows into a set of three Dorr thickeners, where the caustic liquor is separated and the mud is successively washed; between these thickeners the mud is moved by rubber diaphragm pumps; the plant was erected by the Du Pont Engineering Co. The residual calcium carbonate, according to Meade (*Met. & Chem. Eng.* 1915, 13, 289; *J. Soc. Chem. Ind.* 1915, 608) is calcined for repeated use in a rotary kiln and the accumulation of impurities avoided by the addition of 5–10 p.c. fresh lime. A new device by Appareils and Evaporateurs Kestner of Lille, Eng. Pat. 204670, provides a continuous means of agitating and heating the materials under increasing pressures at increasing temperatures, clarifying, filtering, and evaporating the caustic liquor in multiple effect apparatus all with the greatest economy of steam.

Evaporation of the causticised liquor to 60°Tw.—The concentration and finishing are carried on in the same way, and in the same apparatus, viz. cast-iron caustic pots, as already described under the Leblanc process (p. 217, col. 2).

The ammonia soda works were the first alkali works to use for caustic soda liquors the multiple effect evaporators which were long before used by the sugar manufacturers. The process has been successfully and largely used for caustic soda liquors, although they are the most undesirable of all liquors for such an apparatus (see *EVAPORATION*, Vol. II. 691).

The process consists in using the steam produced from the boiling of the caustic liquor at some particular pressure in the first boiler or 'effect,' to cause in the second effect, but at

a considerably reduced pressure, the boiling of another portion of the liquor produced in the first effect; if there be a third effect then the steam produced in the second effect is used to produce in the third effect the boiling of another portion of the liquid produced in the second effect, but of course at a still more considerably reduced pressure, namely, only about 1.5 lbs. per square inch, which is the limit of an ordinary vacuum pump. The number of effects that can be used is limited somewhat by the extraordinary rapid rate at which the boiling-point of caustic soda solution increases on concentration (see p. 213), so that it is not customary to use more than a triple effect, or at most a quadruple effect, and owing to the corrosive action of the caustic solution on metals, the system should always contain an effect boiling under the highest vacuum obtainable, and whereas the number of effects used in a series has been four, it is now most generally two.

Fig. 47 shows a common form of triple effect evaporator.

A is the first effect.

B is the second effect.

C is the third effect.

The shells of these vessels are cast iron and

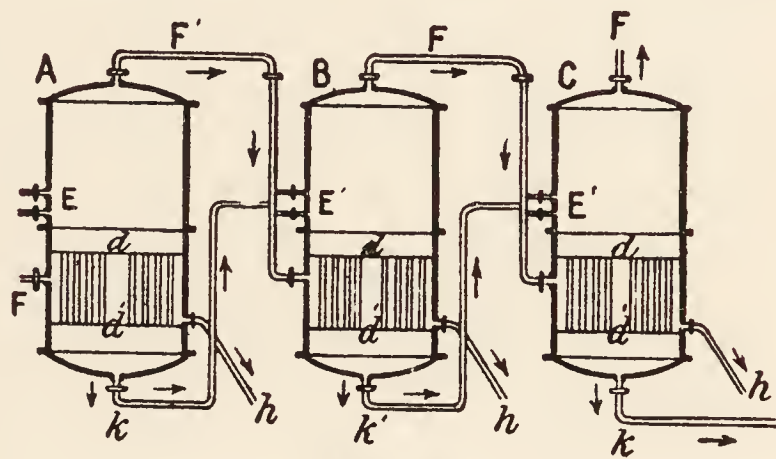


FIG. 47.

the interior is divided by the tube plates d, d' into three spaces, the lower space for the great bulk of the caustic liquor, the top space in minor part for a small bulk of the seething caustic liquor, and in major part for the evolved vapour to deposit the splash and droplets of liquor thrown up from the breaking steam bubbles; the middle space between the two tube plates d, d' is the space for the steam that causes the boiling of the soda liquor, and this space is penetrated by a number of tubes of small diameter and generally by one much larger central tube not shown in the figure, all tubes being expanded into the two tube plates so as to join through the tubes the bottom and the top spaces. When the liquor boils the ascending bubbles of steam in the small tubes carry a considerable quantity of liquor with them, and this liquor returns to the bottom space by the large central tube, where the boiling is relatively less intense per square inch of cross section.

Into each effect caustic liquor is pumped by cocks E, E', E' , until the heating tubes are filled with and submerged in the liquor. The pipe F on the third effect is connected to a condenser and an air pump, and these having been started pressure steam from a boiler is passed by cock F into the heating steam space of the first effect

only. The caustic liquor in A is thus heated, while the heating steam is condensed to water which escapes by the pipe *h* and its control valve which allows nothing but condensed water to pass. To let the air escape which originally filled the steam space a small blow-off cock not shown in the figure is opened; at first a pale bluish jet issues totally unlike steam, but this quickly becomes whiter and more opaque, and when the jet has the well-known appearance of steam the valve is closed or left with only a minute opening. Presently the caustic liquor in A begins to boil and the superheated steam generated mixes with and gradually expels the air which originally filled the vapour space in the upper half of A; the mixed air and vapour passes by a pipe *F'* (of much larger bore than is indicated in the figure) into the steam space of the calandria of B, where it quickly loses its superheat and then begins to condense.

The caustic liquor in B is now being warmed up, and the condensed water produced makes its exit by pipe *h* and its control valve which allows nothing but condensed water to pass, while the air from the vapour space of A and from the steam space of B are allowed to escape by a small blow-off cock (not shown in the figure), and when steam free from air escapes the cock is either closed or left with only a minute opening.

The sight glasses in the upper part of A (not shown in the figure) will now show that the volume of liquor is decreasing, and the continuous feed of caustic liquor must now be started through pipe *E*, and probably also more steam be passed in through *F*.

Whether the liquor in B will boil or not depends either or both upon increasing the vapour pressure in A or decreasing the vapour pressure in B. The vapour pressure in A may be increased indirectly by opening further the valve *F*. The vapour pressure in B may be lowered by opening the valve (not shown in the figure) on pipe *h* from C, which puts the vapour space in B in direct communication with the air pump. By these means the liquor in B is caused to boil, and the superheated vapours generated pass by the main *F* (of very much larger bore than is indicated in the figure) into the steam space in C. Here the liquor tubes quickly remove the superheat and then condense the steam, and both the condensed water and the air that originally filled the vapour space of B and the steam space of C are removed continuously by the air pump. Once this air is removed the control cock on *h* must be considerably closed so as to allow the condensed water and just so much steam and permanent gases as to prevent the last from accumulating, to be sucked out. As the steam is condensed by passing its heat into the liquor in C, the temperature of this liquor is raised.

By the time the liquor in C has approached its boiling-point, it will be seen by the sight glasses in the upper part of B (not shown in the figure) that the volume of liquor in B is decreasing and the valve (not shown in the figure) on the pipe *K* between A and B is opened sufficiently to adequately feed B.

Whether the liquor in C will boil or not depends either or both upon increasing the vapour pressure in B or decreasing the vapour

pressure in C. The vapour pressure in B may be increased indirectly by increasing the steam pressure supplied through *F* to A; the vapour pressure in C may be lowered by running the air pump attached to the vapour pipes *F* (which must be many times larger in bore than is shown in the figure) to its highest limit, by using a sufficient quantity of water in the condenser and by seeing that that water is the coldest obtainable, and by making sure that all joints are air-tight.

When the liquor in C has been boiling some time, the cock on *k'* between B and C (not shown in the figure) must be opened sufficiently to keep the liquor level steady in C.

Samples of liquor may be drawn from C by a small vessel underneath it (not shown in the figure), provided with two valves, one between it and C, and one between it and the air, only one of which may be open at a time. When the sample has the required specific gravity the caustic is drawn off through liquor pipe *k* by a suction pump (not shown in the figure).

The evaporator having been started may be run continuously with a minimum of attention.

The speed at which evaporation proceeds in any effect depends on the number of temperature degrees that the condensing temperature of the steam on the outside of the boiling tubes is above the boiling-point of the liquor found on the inside of the tube under the total pressures to which it is subject. If the immense volume of generated vapour is in any way prevented from the freest passage through the tubes *F*, *F'*, and through the liquor to the steam space above, then the speed of evaporation is reduced. According to Annual Report Soc. Chem. Ind. 1917, it is possible by reducing the static level of the liquid in these evaporators to increase the amount evaporated by as much as 50 p.c. in a given evaporator.

Another type of multiple effect evaporator is Kestner's climbing film evaporator, a curtailed section of one effect of which is given in Fig. 48.

There are shown by the horizontal section inserted in the middle of vertical section 14 tubes about 2 ins. in diameter, which are extraordinarily long, viz. 23 ft. 6 ins. The amount of caustic liquor required to fit the effect for work is very small, namely, about 3 cub. ft.; except for a top cushion of air it fills the small bottom chamber and also about 3 ft. of the long tubes, and that is all. The length of the heating space between the two tube plates is figured 23' 0", and the steam inlet and distilled water drain are named in the figure. The steam being admitted and the air driven out through an air cock (not shown), but situated just under the top tube plate, the caustic liquid in the tubes soon reaches its boiling-point, and the bubbles of steam generated carry a little of the liquor higher up the tubes, as the boiling becomes more energetic, until a small quantity in a concentrated condition is blown through the tops of the tubes, and striking the baffle or the inside of the spray separator chambers marked 3' 0" and 4' 6", it trickles down to the concentrated liquor outlet and so runs away. It cannot re-enter the tube or any other tube, because of the blast of steam coming from them, and because the tube plate is surrounded by a drainage channel leading to the concentrated

liquor outlet, and therefore the separator chambers contain no stock of liquor. The small amount of spray caught in the upper separator chamber, being weakened by a small condensa-

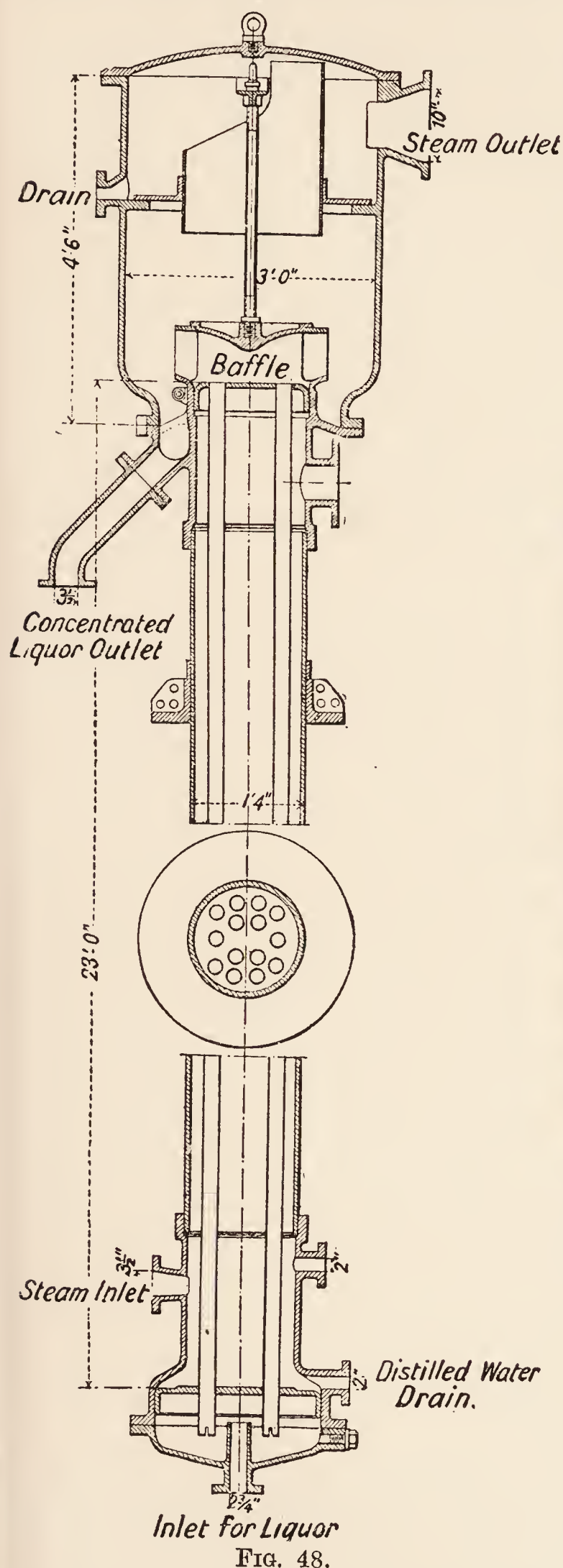


FIG. 48.

tion of the vapour, may be run by the drain to a suitable store-tank. The whole effect is suspended by the angle brackets shown just under the words 'concentrated liquor outlet.' The same shaped effect is used for all subsequent

effects except that (1) the 'steam inlet' is then banked up, (2) the vapour from the previous effect is admitted by the large diameter flanged pipe shown on the right side and not far below the top tube plate, (3) the air outlet cock is shifted to the bottom end of the effect, as the flanged pipe marked 2" not far above the distilled water drain, and (4) the 'inlet for liquor' is not connected to the caustic liquor pump, but to the concentrated liquor outlet from the previous effect.

Fig. 49 shows a quadruple effect Kestner evaporator, of older pattern than Fig. 48 in the separator chambers. It shows the great height of the effects and the ladders that connect

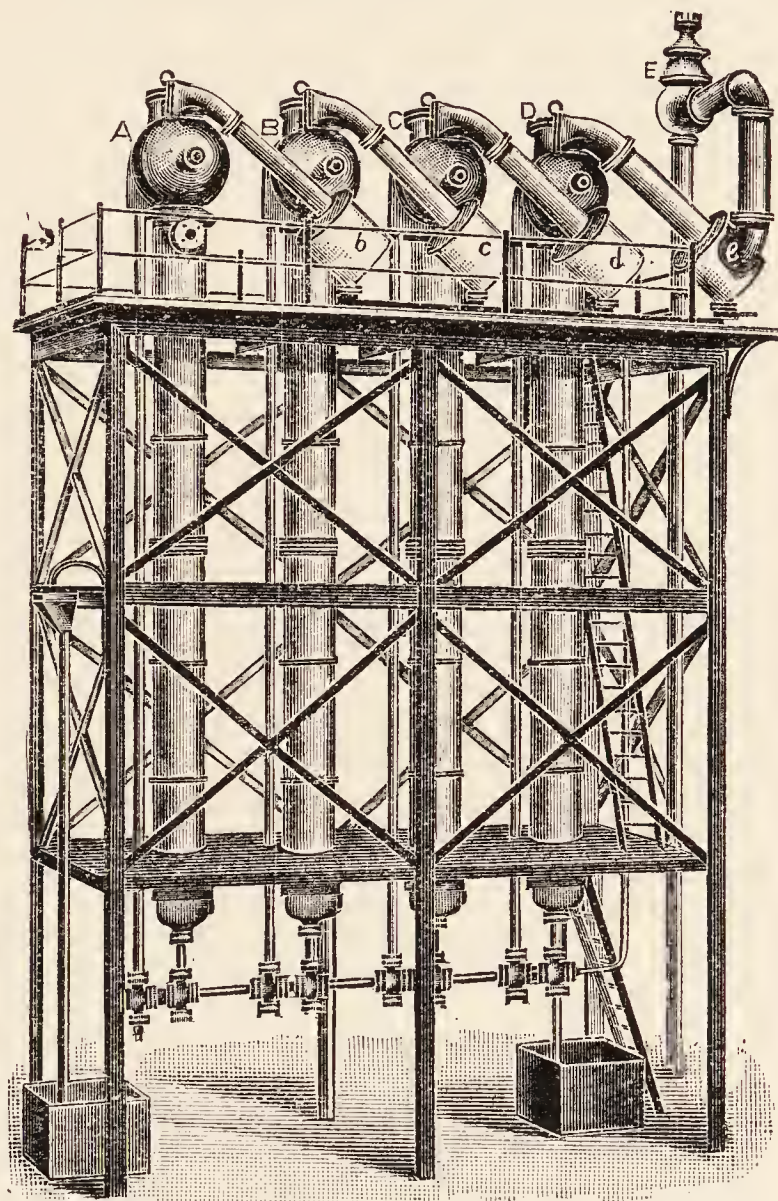


FIG. 49.

together the three working floors; also a couple of liquor tanks. The first effect is A, then B, C, and D; the slanting pipes are the vapour pipes from the working space of each effect to the steam space of the following effect, and the vessels b, c, d, e are spray catchers. E is the water condenser for creating and maintaining the vacuum on the working space of the last effect. Owing to the rapid rise of the boiling-point of the concentrating caustic liquor (see p. 213, cols. 1 and 2), the steam pressures in the several effects falls very rapidly, in the first effect 52 lbs. absolute is required, and this produces in the second effect 35 lbs. absolute, in the third effect 18½ lbs. absolute, in the fourth effect 7½ lbs. absolute, while the vacuum on the caustic soda in the fourth effect is only 1½ lbs. absolute. The arrangement of the caustic-liquor pipes at the bottom part of the plant is not shown

explicitly, but essentially they are the same as in Fig. 47. The climbing film evaporator has very high liquor velocities, and hence a very high heat transmission per square foot of tube (Applied Chem. Report, 1917, p. 11).

The two types of multiple effect evaporators just described are satisfactorily used to evaporate the liquid up to 60°Tw., because the residual sodium carbonate from the causticising then remains in solution. If the evaporation were carried further then sodium carbonate monohydrate would separate from the boiling liquid and encrust and fill up the pipes and passages. The liquor has therefore to be run out of the last effect before it deposits carbonate, and allowed to cool in the collecting tank till the bulk of the dissolved carbonate has crystallised out. The clear and much colder liquid is then ready for further treatment.

Evaporation to 105°Tw.—For the next further concentration of the clear 60°Tw. liquor, the same types of apparatus may be used, only that the number of effects are reduced to at most three, probably two, because the rate of temperature rise of the boiling-point with further increase of concentration now becomes very great. Owing to the smaller but continuous deposition of carbonate crystals it is customary to make special arrangements for collecting the crystals.

With the short tube evaporators the crystal collectors take the form of large conical bottom chambers where the crystals settle, and the liquor pipe feeding the following effect, if there be one, is arranged to take as few salts as possible. The effects are filled with the liquor at 1.3 sp.gr. and concentrated, adding more fresh liquor continuously to make good the loss by evaporation. Eventually when the last effect of the evaporator is full of liquor at 1.4–1.5 sp.gr., as may be required, the bottom valve is opened and the whole contents, liquor and salts, allowed to fall into a settler or on to a filter bed. The salts are separated and the liquor is pumped to the store tanks feeding the finishing pots. From time to time the whole apparatus has to be stopped, emptied and washed to remove the crusts of carbonate. To render such apparatus more continuous, there are provided under the large conical bottoms (1) small closed vessels, which can be opened by valves either to the salt-collecting cone or to the air, so that the crystals may be removed at any time without interfering with the running of the apparatus; or (2) a small closed filter box suitably fitted; or (3) automatic arrangements have also been invented for continuous removal of the salts from the evaporators, and it is understood are used to some extent. These apparatus also require stopping and washing at intervals.

With the long-tube Kestner type of evaporator, which holds practically no stock of liquor, the usual method of work is to start with 1.3 sp.gr. caustic liquor in a stock tank, and to circulate it round and round, through the evaporator and back to the stock tank, until the whole is up to 1.4–1.5 sp.gr., and the salts have deposited in the stock tank. After a certain time these tubes also become encrusted with carbonate, to remove which all the liquor is drawn off and water is pumped through the effects.

A recent arrangement, known as Kestner's salting type evaporator, consists in removing the superimposed spray separator chambers, shown in Fig. 48, and a pipe and valve substituted, through which the vapour and turbid liquor are discharged into a large vessel, around which several similar evaporators are similarly connected. The upper part of the central vessel acts as a vapour separator, and the vapour is used for heating another group of effects; the lower part of the central vessel acts as a storage and settler for the turbid liquors, and the clarified liquor enters the effects again for further concentration without any pause. The settled salts are withdrawn periodically or continuously, and may be drained and washed before final removal. Sooner or later the heating tubes become scaled, and then one only out of the group of effects is separated from the rest of the apparatus by closing inlet and outlet valves, the liquor is pumped out, the tubes washed, and the effect restarted, and so any one of the effects may be thoroughly cleaned without stopping the rest of the evaporator plant (Pat. 110921; J. Soc. Chem. Ind. 1917, 1263; Reavell, J. Soc. Chem. Ind. 1918, 172 T.).

Caustic soda solution as made in any of the above evaporators is sold to some extent, usually in one of three strengths: 90°Tw., containing 32.2 p.c. Na_2O ; 100°Tw., containing 36.2 p.c. Na_2O ; or 105°Tw., containing 38.2 p.c. Na_2O . These solutions are carried either in strong welded iron drums or in iron tank waggon.

Evaporation to 60 p.c. Na_2O , solid.—The caustic soda solutions of 90°–105°Tw. are frequently evaporated further by the aid of high-pressure steam, and a vacuum on the vapour from the caustic liquor, occasionally in a double effect evaporator, more generally in a single effect evaporator. Owing to the corrosive nature of the very strong liquors it is now necessary to use cast-iron tubes, and the joints are made by machined faces being mechanically pressed together by screw joints. These tubes in the Kestner single effect finishing evaporator are 2 ins. bore and 15 ft. long (see Annual Report Soc. Chem. Ind. 1917, 9). The concentration may be carried on with high pressure steam until the liquor sets quite solid on cooling and the process is more economical than by a direct fired pot (Reavell, J. Soc. Chem. Ind. 1918, 176). Such a product tests 60 p.c. Na_2O , and hence contains 73 p.c. of the lowest known hydrate $\text{NaOH}\cdot\text{H}_2\text{O}$, which melts at 64°, and 27 p.c. of NaOH anhydrous (see Notes on Modern Evaporators, J. Soc. Chem. Ind. 1917, 70). This product corresponds to the old-fashioned 'cream caustic' of the Leblanc alkali makers, but differs from it by its exceeding purity.

Evaporation to fused caustic.—Any of the above steam evaporated liquors can be rendered completely anhydrous by evaporation in open cast-iron caustic pots essentially as already described under caustic soda by the Leblanc process (p. 218, col. 2, last three pars.), but simplified greatly as regards the removal of impurities, since the only essential impurity is sodium carbonate. The anhydrous caustic soda produced contains only about 2 p.c. of impurities; its commercial test is 76–77 p.c. Na_2O .

Causticising Lieber and Walz's sodium carbonate.—Another source of sodium carbonate specially adapted for conversion into caustic soda was afforded by the process of Lieber in 1867 (Berichte, 8, 49). He mixes nitre and calcium carbonate and heats the mixture in retorts through which steam was passed; nitrogen oxides are evolved from which almost the theoretical amount of nitric acid is obtained, and the residue in the retort is a mixture of sodium carbonate and lime, which only requires lixiviation to obtain a solution of caustic soda.

Walz described the same method in Wagner's Jahresb. 1869, 182.

(3) *The manufacture of caustic soda by electrolytic methods.*—The action of an electric current on a solution of salt to produce an alkaline solution around the kathode was discovered by Dr. Cruikshank, of London, in 1800, and in 1801 Prof. Simon, of Berlin, noticed the smell and bleaching properties of the liquor around the anode.

The manufacture of caustic soda by the electrolysis of brine was first suggested by Eng. Pat. 13755 of 1851 by Charles Watt, but as the electricity had to be made by a chemical battery consuming zinc and acid the process was useless commercially.

In 1866 the first dynamo machine was made by Werner Siemens, and in 1872 Gramme made the first dynamo machine for electro-plating, and they were followed in 1877 by Siemens and Halske, making their first dynamo for electrolytically refining copper.

In 1884 Höpfner patented by D. R. P. 30222, among other claims, the use of a depolariser around the cathode as red lead, iron oxides, or manganese dioxide in order to reduce the voltage and to prevent the generated hydrogen from agitating the strong caustic liquor around the cathode, and the process was examined by the Chemische Fabrick Griesheim. They soon found it to be impracticable, but other methods were tried, and by 1890 the Griesheim-Elektron Works were manufacturing caustic soda by a diaphragm cell. In England other practical processes quickly followed, Richardson and Holland in 1890, Eng. Pat. 2297; Castner in 1892, Eng. Pat. 16046; Hargreaves and Bird in 1892, Eng. Pat. 18871.

Special cells.—A classification and description of the various types of cells is given in vol. ii. pp. 194–199, which see. Additional notes are:

Acker cell.—The lead sodium alloy obtained was blown with steam in the absence of air to obtain molten caustic soda (Eng. Pat. 14269 of 1898).

Hargreaves-Bird cell.—Besides vol. ii. p. 196, see this volume under *Sodium carbonate*, p. 160, col. 1).

Nelson cell is a modification of the Hargreaves cell, in that the two cathode-diaphragm sheets are joined at the bottom and made continuous (1908), and steam was blown into the cathode chamber to prevent the porous diaphragm blocking up and to dissolve the caustic soda hydrates as they were formed (1913), and by specially preparing the graphite anodes to increase their durability, and, lastly, by adding an automatic brine feed regulator to the anode cell. Plants have been erected in all

parts of the world, the total ampere capacity being nearly 8 million (U.S. Pat. 1149210 of 1915; J. Soc. Chem. Ind. 1915, 969). The outer case of the cell is a bent steel plate parallel to the cathode-diaphragm. The anode cell is covered by an inverted slate box, forming a chlorine compartment, and the top of it is perforated to carry the anode stems, which are 2½ ins. diameter, and the bottom end is screwed, and screwed into the anodes proper, which are graphite blocks 4 ins. by 4 ins. and 17 ins. long, of which only 15 ins. is immersed in the brine. The brine is purified before use from iron, lime, magnesia, and alumina; the float regulating its admission carries a blunt knife edge which presses, or does not press, on a rubber tube supplying the brine. A cell with 14 anodes takes 600–1100 amps. with a voltage of 3·7. The liquor obtained contains 10–12 p.c. NaOH and 14–16 p.c. NaCl. The cells are cleaned every 6–8 months and provided with new diaphragms. The cell is said to be unique in that it may be stopped at any time without harm. The anodes last 2 years, the cathodes 2–5 years, and the outer tanks are expected to last 20 years. The attendance is only one man per 200 cells, and in West Virginia one man has managed 480 cells. The liquor is especially free from hypochlorites, and, therefore, the evaporator tubes last not uncommonly for 2 years. The chlorine is 99 p.c. purity. The electrical efficiency is 86–90 p.c. (Trans. Amer. electrochem. Soc. 1919, 35, 239).

Allen-Moore cell is a modification of the Hargreaves cell (see Fig. 11, vol. ii. p. 196) in that the outer case of the cathode compartment is partly open at the bottom to the air for the escape of the hydrogen, and the cathode is spongy, being made of many layers of iron wire or wire gauze, or iron turnings resting on an iron grid. Billiter, in Monographien u. angew. Electrochemie, 41, pp. 241, 245, 249, severely criticises this cell; but the Applied Chemistry Report of 1920, p. 289, states that it has been used extensively in America, and that it is now being introduced into France (Eng. Pat. 4269, 1900; U.S. Pats. 680191, 1901; 703289, 1902; 716804, 1902).

Gibbs cell is a modification of the Hargreaves cell, in that the outer cell and the anode cell are cylindrical and concentric, but the supporting perforated cathode plate is deeply corrugated vertically and slightly corrugated horizontally; and the diaphragm is thicker at the bottom so as to compensate for the greater hydrostatic pressure at the bottom of the brine cell (see Monographien u. angew. Elektrochemie, vol. 41, p. 191; Eng. Pat. 27830 of 1907; U.S. Pats. 87064, 1176540, and 1176541, both of 1916). In these last two patents A. E. Gibbs is the assignor for the Pennsylvania Salt Manuf. Co. of Philadelphia; the cathode is washed with an auxiliary brine flow that does not pass through the diaphragm (J. Soc. Chem. Ind. 1916, 547). This cell is used in this country by the United Alkali Co. (Clayton, J. Soc. Chem. Ind. 1921, 443, R.).

Finley cell.—The cathode liquor contains 7 p.c. NaOH.

Mercury cathode cells.—The soda solutions produced by the decomposition of the sodium amalgam are very pure and free from NaCl, and they generally contain about 20 p.c. of

NaOH. The concentration of this liquor is therefore not complicated by the deposition of salt or sodium carbonate, and as the liquors are so strong the evaporation plant is both simplified and reduced in size.

Glocken cell.—The soda solution obtained contains 6–12 p.c. NaOH and 16–20 p.c. NaCl (Chem. Zeit. 1901, 1171). These liquors are evaporated like the liquors from the diaphragm cells (see p. 226, col. 2, *Evaporation, &c.*).

A modification of the Glocken cell has been patented by the Society of Chemical Industry of Bale, 25118, 1909, the main point of which is the continuous saturation of the brine by causing the fresh electrolyte to flow from an upper to a lower electrode through a layer of solid salt fed in a special manner. The advantage consists in obtaining a higher strength caustic soda with a good current efficiency.

Electrolytic analysis.—In the laboratory electrolytic cells with mercury cathode have been constructed for analysing liquids containing alkaline halides and determining both anion and cation (see Vol. I. 309 and 322).

Anodes.—The first anodes used were made from retort carbon, either in cut pieces which are very expensive, or else in large irregular pieces with lead cast on to them to joint them up to make large electrodes or to make connections to them, as in the Eng. Pats. 26059 (1896) of Connor, and in 25519 (1897), J. Hargreaves. Castner (Eng. Pat. 19809, 1893) by heating pressed electrodes with a heavy current volatilised the residual hydrocarbons, &c., contained in them, and converted them into a body resembling graphite, which was very resistant when used as an anode. Girard and Street (Fr. Pat. 231211, 1893) electrically heated pressed carbon rods by electric arcs for the same purpose. Acheson (U.S. Pat. 542982, 1895) recognised the purity of the above electrically heated carbons, and with the aid of large supplies of electric power at Niagara Falls manufactured graphite in various forms, including graphite electrodes, which are highly resistant when used as anodes in brine electrolysis, and they also have a reduced electrical resistance, and, further, may be extraordinarily easily cut to any desired shape, including even the cutting of screw threads (Monographien ü. angew. Elektrochemie, vol. 15, Künstlicher Graphit by Fitz-Gerald, 1904).

Platinum anodes have been used by Kellner and others. Better than platinum is an alloy with 10 p.c. of iridium, with all traces of ruthenium removed. The wires are mounted in various ways to economise the metal and to reduce the electrolyte resistance. These results are improved by using very short wires as conductors, which are sealed into the sides of glass tubes, while the actual anode is made of the same metal in the form of foil only 0.0075 mm. thick, the two being welded together (Zeit. f. Elektrochemie, 1902, 147). A further improvement is to coat them with black spongy platinum (Jahresb. d. chem. Tech. 1906, 441). Besides being more expensive than carbon electrodes, they also have the disadvantage of requiring a higher voltage.

In 1895 Blackmann (D. R. P. 92612) prepared electrodes of magnetic oxide of iron. In 1902 the Griesheim Elektron Alkali Works patented (D. R. P. 157122) the heating of ferric

oxide (purple ore) in an electric arc furnace, and casting the fused mass into electrodes of 30 kg., and assert that their cost is but one-fifth that of carbon anodes, they have an unlimited life, yield a chlorine free from carbonic acid, and require a smaller voltage than platinum anodes. In 1906 they obtained (D. R. P. 193367) for adding to the electrically heated ferric oxide, while in fusion and to compensate too large a reduction to ferrous oxide, further quantities of ferric oxide to convert all into magnetite, Fe_3O_4 , and also for making cores of good metallic conductors. Lepsius wrote (Ber. deutsch. Chem. Ges. 1909, 2892) that after the Griesheim works had built a special factory for making carbon anodes, they had recently decided to entirely replace the carbon anodes by magnetite anodes. In 1910 the Chem. Fabrik Buckau (D. R. P. 235307) prepared magnetite electrodes by heating steam in iron pipes so that the magnetite compressed itself in its formation. In 1917 (Trans. American Electrochemical Soc. 213), it is stated that when the war of 1914 cut off the supplies of magnetite electrodes from Germany to America, they were manufactured in America, and the extreme brittleness of the electrodes had been remedied by making the cooling more gradual and by adding a few per cents. of copper oxide.

Anodes have also been made from manganese dioxide (D. R. P. 235234, Siemens Halske, and 235207, Chem. Fabric Buckau), by igniting mixtures of native manganese dioxide and solutions of manganese nitrate. By forming these anodes around a rod of lead dioxide they have a greater electrical conductivity.

Ferrosilicon anodes were used by Hoepfner (D. R. PP. 68748, 1890, and 77881, 1891).

Lead dioxide anodes were prepared by Ferchland (D. R. P. 140317) by electrolysing solutions of lead nitrate kept basic by lead carbonate, the deposit occurs at the anode.

Evaporation of electrolytic caustic soda solutions, especially those containing salt.—Comparing the various types of cells, Bakeland (Met. and Chem. Eng. 1914, 12, 557, 561, 566) wrote that diaphragm cells are cheapest to construct and operate provided that no exception be taken to the sodium chloride in the caustic soda obtained, but the separation of this sodium chloride and the evaporation of the weak caustic liquors, which are produced by some diaphragm cells and by the Aussig gravity or bell cells, often lead to most serious expenses.

The general method of evaporation is to first evaporate in multiple effect vacuum apparatus and then to finish in open cast-iron pots. When using a solution containing per litre 120 grms. NaOH and 100 grms. NaCl the process is complicated by deposits, corrosion of the evaporating plant, and by the high boiling-points of the liquor. Quadruple effect evaporators are not possible; triple effect evaporators can only be used under favourable conditions; double effect evaporators are the most economical. Up to 40°Be. the tubes may be made of steel, charcoal iron, or nickel steel, but above that strength cast iron is the only obtainable material that will stand; copper has been used, but it will not stand the wearing action of the salt crystals deposited (Mantius. Trans. Amer. Electrochem. Soc. 1914, 26, 215).

Cast iron is not used for the lower strengths of liquor, because it does not transmit heat so well as mild steel, and hence would necessitate a greatly increased size for the evaporator. There is great difficulty in obtaining a uniformly satisfactory steel, and the lasting qualities cannot be guaranteed; the steel becomes cracked irregularly, but it begins at the expanded joints where the tubes are fitted into the tube plates; tubes that stand lime causticised liquors will not stand electrolytic caustic liquors; thorough annealing of the steel after the mechanical processes of forming the tubes reduces or removes this brittleness (Voss, from Fischer's *Jahresb. d. chem. Tech.* 1907, 371).

The corrosive action of caustic soda liquors on steel plates, and on the steel tubes of vacuum evaporators, has been discussed by Stromeyer and by Worsley (*Chem. Trade Journal*, Dec. 22, 1917, and Jan. 26, 1918); also by Jones (*Trans. Faraday Soc.* 17, 102).

For explanations of the embrittling of iron by caustic soda, see Andrew (*Trans. Faraday Soc.* 9, 316).

At the temperature of the electrolytic apparatus the liquors are generally nearly saturated solutions of salt, but at the temperature of the first effect of the multiple effect apparatus the solution is not saturated with salt, and therefore very little salt separates in that effect.

When evaporating the liquor in submerged tube vacuum evaporators beyond the stage when the salt first begins to separate, it separates in small crystals which remain in suspension owing to their low sp.gr. and to the high sp.gr. of the mother liquor, and are carried through the heating tubes repeatedly until they gradually build up and become large enough to settle out, when they are easily separated. The Swenson Evaporator Co. of Chicago have utilised these properties in their evaporators (*Met. and Chem. Engineering*, 18, 543, and 19, 633).

In submerged tube vacuum evaporators the amount of the submergence, by its effect on the boiling-point of the solution, has a large effect on the scaling and scouring of the tubes by the separated salt, namely, shallow submergence increases these troubles, and deep submergence reduces them (*Met. and Chem. Engineering*, 18, 187); but deep submergence by reducing the velocity of the liquor in the tubes reduces the evaporative capacity (*Annual Report*, 1917, *J. Soc. Chem. Ind.* p. 11).

Kestner's salting type evaporator has been described (p. 224, col. 2).

Kestner's single effect finishing evaporator has been described (p. 224, col. 2, *Evaporation*, to 60 p.c. Na₂O). In order to remove the metallic impurities, as iron, from the concentrated caustic liquor of 50–60 p.c. Na₂O from the vacuum pans, it is electrolysed by Kipper (*U.S. Pat.* 1227453, 1917) in a somewhat complicated apparatus between nickel electrodes at 80–175°C. with 0.5 to 1.5 amps. per sq. in. (*Met. and Chem. Eng.* 17, 90, and *J. Soc. Chem. Ind.* 1917, 711).

Evaporation to powder caustic.—A still higher strength product, viz. 90 p.c. NaOH, is obtained, according to D. R. P. 182201, by heating a solution of caustic soda of 1.53 sp.gr. in a vacuum pan fitted with an agitator

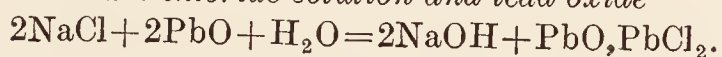
up to a final temperature of 180°C. The liquor becomes thick and then solid, and the agitator breaks this up into a dry powder (Fischer's *Jahresb. d. Chem. Tech.* 1907, 364).

Evaporation to the crystallisation of anhydrous caustic from molten monohydrate NaOH·H₂O.—A novel method of obtaining anhydrous caustic soda was patented by Griesheim-Elektron (*Eng. Pat.* 29491; see *J. Soc. Chem. Ind.* 1910, 488, 817, 1205). The solution is evaporated until it contains 90 p.c. NaOH, and then by cooling with agitation it begins to deposit crystals of anhydrous NaOH. When the temperature of 220° is reached the mixture of crystal and mother-liquor is getting too stiff to work, so it is thinned by adding one-sixth portion of 70 p.c. NaOH solution at a temperature of 130°. The mixture has a temperature of 170°, and is then centrifuged. The crystals obtained contain 99 p.c. NaOH, and they amount to 80 p.c. of the original strong hydroxide. That anhydrous caustic soda can be crystallised from its solution in molten monohydrate was predicted by Pickering in his determination of the equilibrium curve for caustic soda and water (*Journ. Chem. Soc.* 1893, 890).

References.—Summaries of the development of the electrolytic caustic soda manufacture in Germany, England, and France are contained in *Monographien ü. Angew. Elektrochemie*, vol. 12, by Ferchland (1904); vol. 28, by Kershaw (1907); and vol. 42, by Pitaval (1912).

4. *The preparation of caustic soda by methods of minor importance chronologically arranged and headed by the materials employed in the final reaction.*

Sodium chloride solution and lead oxide



In 1773 Scheele noticed that common salt is (partially) decomposed by lead oxide, caustic soda and lead oxychloride being formed as according to the above equation.

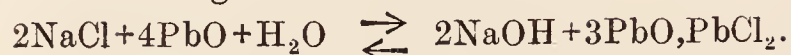
This process was at first considered one of the most favourable for the manufacturing of caustic soda, and was worked both in France and England, where many patents were taken for it. It was the process first employed by Losh at Walker-on-Tyne, at the same works where also one of the later patents (1869) belonging to this class, Bachet's, who used a mixture of two parts of lead oxide and one of slaked lime, received a serious trial in 1870, but with hardly more success than formerly, although he converted 47–50 p.c. of the salt into caustic soda. The incompleteness of the reaction is the principal obstacle to this process. A later patent is Knab's (*Eng. Pat.* 3082, 1877). The Société Anonyme Lorraine Industrielle (D. R. P. 23791) separates the caustic from the lead oxide by alcohol. Romiquières (*Eng. Pat.* 14977, 1888) dissolves finely-divided lead in caustic soda by means of a current of air; the solution of Na₂PbO₂ thus obtained is treated with NaCl, which precipitates lead chloride and the decanted liquor contains a correspondingly increased amount of caustic soda.

Berl and Austerweil (*Zeitsch. Elektrochem.* 1907, 165) describe the reaction as reversible, and give two equations:

1. For 'normal concentration'—

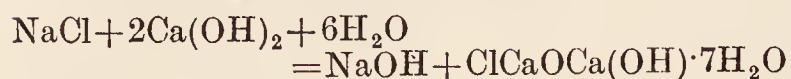


2. For higher concentrations—



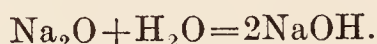
The conversion of NaCl to NaOH at 18°C. is 50 p.c., at 48°C. is 43 p.c., at 74°C. is 37 p.c.

Sodium chloride and slaked lime

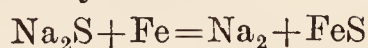


(calcium oxychloride). This reaction has probably never been used for making caustic soda, but by the additional reaction of the absorption of carbon dioxide from the air it has been used for making sodium carbonate (p. 159, col. 2, last par.).

Sodium monoxide (crude) and water



In 1778 Malherbe roasted sodium sulphate with charcoal and scrap iron. The first reaction produces sodium sulphide, and the following reactions probably followed:



and the furnace gases would burn the sodium to Na_2O . On extracting with water, caustic soda passed into solution along with many impurities, and on this account the fused mass was allowed to absorb carbon dioxide from the air, and was then worked for sodium carbonate (p. 160, col. 1).

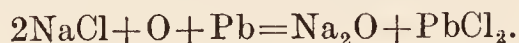
In 1828 Siemens also used the process on a large scale, with the modification of adding some manganese dioxide.

In 1854 Blythe and Kopp also worked the process at Church, near Manchester, and it was considered to be capable of great development.

In 1859 Brown and Robinson (Pat. 3044) proposed to use the process for the preparation of caustic soda, but the liquors always contained too much undecomposed sulphide.

Macfarlane (1863), Letelié and Dow (1870), Hargreaves and Robinson (1872 and 1873), also used this process.

In 1908 (Pat. 23689) Vournasos prepared the crude sodium monoxide in two ways: (1) 100 parts of salt and 200 parts of lead is heated to not above a red heat with access of air

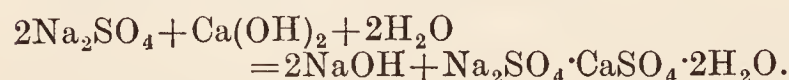


(2) Salt and lead oxide are heated together



In either case the product when extracted with water yields a solution of caustic soda (J. Soc. Chem. Ind. 29, 151).

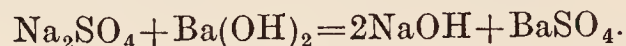
Sodium sulphate and slaked lime



In 1789 Delius proposed this method, and many other chemists followed him, and some sodium carbonate was made out of the caustic thus produced. In 1865 Hunter added the action of pressure. But the change is extremely imperfect as proved by Hill (Chem. News, 27, 165), and experiments made by Lunge (Dingl. poly. J. 238, 69), and by Cross and Bevan (*ibid.* 213, 137), confirm this. The highest conversion of the sodium sulphate into caustic soda was obtained by Lunge, using the boiling temperature at 5 atmospheres pressure and 25 parts of water to one part of sodium sulphate; the yield was 31.7 p.c. The existence of

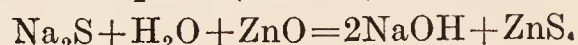
double salts has generally been disregarded, but their formation doubtless profoundly affects the reaction.

Sodium sulphate and barium hydroxide



This reaction was adopted by Fuller in 1819, and was utilised by Schubert (J. pr. Chem. 26, 117) to obtain pure caustic soda. The reaction is complete, as caustic soda solution does not act upon barium sulphate (H. Rose). For manufacturing processes the process fails, because the conversion of the barium sulphate produced into barium hydroxide has been found too cumbersome and costly.

Sodium sulphide (solution) and metallic oxides



In 1804 (Pat. 2793) Clayfield proposed zinc oxide. This was repatented in 1870 (No. 2399) by Parnell; in 1871 (Nos. 1531 and 2024) by Crockford; in 1887 (Ger. Pat.) by Lalande, who found it to effect the desulphurisation very well when tried at the St. Gobain works, but the separation of the ZnS and the regeneration of ZnO were found to be too troublesome. This process has found for many years extended applications for purifying Leblanc's liquors from sodium sulphides, and in these cases no attempt is made to use the zinc sulphide produced (*see* p. 170, col. 1, (1)).

In 1804 (Pat. 2793) Clayfield proposed lead oxide PbO.

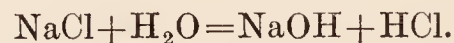
In 1829 Prückner obtained a prize from the St. Petersburg Academy of Sciences for a process using coppersmiths' scales, mostly Cu_2O cuprous oxide. The same oxide was used by Pool (Pat. 8304 of 1839). Hunt (Pat. 8356 of 1840) also used cuprous oxide, obtaining it by treatment of cuprous chloride with lime. Possoz (Compt. rend. 47, 848) used Prückner's method. Burton (Pat. 1352 of 1862) patented the use of cuprous oxide; and Bazin and Wilden (Fr. Pat. April 3, 1876) did the same.

In all these cases much more than an equivalent of the metallic oxide is required for effecting a complete decomposition of the sulphide.

In 1838 (Pat. 7879) Wilson used hydrated ferrous hydroxide, agitating by blowing steam into the mixture. The ferrous sulphide produced was again brought into the process, both as regards its iron and its sulphur contents.

In 1862 (Pat. 1352) Burton used ferric oxide, and the same was used in 1876 by Bazin and Wilden (Fr. Pat. April 3). In this case the reaction is complicated by the oxygen liberated during the conversion of the ferric oxide into ferrous sulphide. The reaction is also slow and incomplete.

Sodium chloride at a red heat and steam



In 1837 (Pat. 7426) Sheridan proposed this process, and in 1861 Gillard (Pat. 1790) did the same; also Swinburne in 1862 (Pat. 3134), and Gillard in 1865 (Pat. 1914).

In 1863 (Pat. 91) Powers and Dale repeated the above with the addition of oxides of iron, aluminium or manganese.

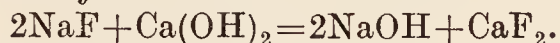
In 1865 (Pat. 3340) Laurent, and in 1866 Weldon, proposed the above reaction.

In 1884 (Pat. 14866) Bolton repeated the above with the addition of barium and strontium

sulphate, and on lixiviating caustic soda was obtained.

In 1885 Spring (Ber. deutsch. Chem. Ges. 1885, 345) records that in $1\frac{1}{2}$ hours heating (to an unstated temperature) that the reaction proceeded to the extent of 0.0087, and that as the reaction proceeds the speed of the reaction rapidly decreases, and that a mixture of $10\text{NaCl} + 1\text{NaOH}$ evolves a trace of acid even at 235° , but at 500° it evolves the acid steadily.

Sodium fluoride and slaked lime



In 1837 Spilsbury and Maugham (Pat. 7277) described this process, which is conducted between the two very slightly soluble substances in presence of boiling water; the clear settled liquor is a solution of caustic soda. The sodium fluoride they obtained as a precipitate by treating a salt solution with hydrofluoric acid. In 1866 (Pat. 628) Weldon described the same process.

In 1857 and in 1864 Ward and Wynautes patented (3185 and 1375) the preparation of crude sodium fluoride, by heating finely ground soda felspar with sufficient fluorspar CaF_2 , or cryolite Na_3AlF_6 , to convert the soda into sodium fluoride, and also with chalk and lime; the mass fritted; extraction with water then gave a solution of caustic soda. The process was found too expensive.

Brochon, in Fr. Pat. 208754, describes the preparation of sodium fluoride; heated fluorspar is decomposed by steam and the evolved hydrofluoric acid gas is made to act upon salt either fused or in solution.

Krautz, in Ger. Pat. 65576, describes the obtaining of sodium fluoride by a complicated process from sodium fluosilicate, and the decomposition of the sodium fluoride by lime as above described.

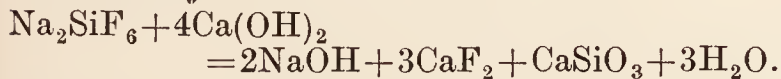
Le Chatelier, in 1858, patented the preparation of sodium fluoride by heating sodium silicofluoride $\text{Na}_2\text{SiF}_6 = 2\text{NaF} + \text{SiF}_4$.

Karcher and Tessie de Motay, in 1865, patented a method of preparing a solution of silicofluoric acid, and then proceeded to Le Chatelier's method. A factory, working on this patent, existed for some years up to 1870, near Saargemünd, and the process seems to have given better results than might have been anticipated; but the various reactions on which it is based are too incomplete especially the main reaction for the conversion of the sodium silicofluoride into sodium fluoride.

Claus, in 1869 (Pat. 3745), prepared sodium fluoride for this reaction, by heating sodium silicofluoride with sodium sulphide

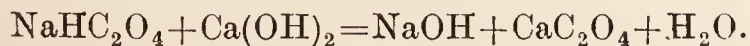
$\text{Na}_2\text{SiF}_6 + 2\text{Na}_2\text{S} + 2\text{H}_2\text{O} = 6\text{NaF} + \text{SiO}_2 + 2\text{H}_2\text{S}$.
The residue heated with lime and water gave a caustic soda solution quickly and completely.

Sodium fluosilicate and slaked lime



This method was first used in 1837 by Spilsbury and Maugham (Pat. 7277), the sodium silicofluoride being obtained from salt and hydrofluosilicic acid. In 1840 the process was used by Authou with good results (Wagner's Jahresh. 1863, 228).

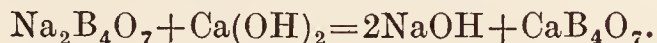
Sodium acid oxalate and slaked lime



In 1838 (Pat. 7873) Samuel proposed this process, the decomposition being effected at 100°C ., and the acid sodium oxalate being obtained by adding oxalic acid to brine. The oxalic acid was recovered from the calcium oxalate by treatment with sulphuric acid. The same process was patented in 1855 (Pat. 159) by Margueritte, and in 1866 (Pat. 629) by Weldon.

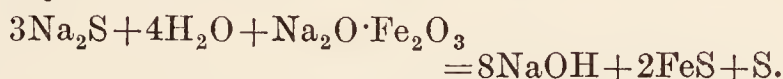
The same end reaction was used by Bang in 1864 (Pat. 2864), by Knab in 1877 (Fr. Pat. Jan. 3), and Marchand (Fr. Pat. 213354).

Sodium borate and slaked lime, say



In 1855 this method was patented by Margueritte, who prepared his sodium borate by heating salt with boric acid in presence of steam. In 1889 Garroway proposed to also use nitre-cake in preparing the sodium borate.

Sodium sulphide solution and sodium ferrite, say

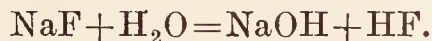


In 1859 (Pat. 1370) Arrott treated moist sodium ferrite with a solution of sodium sulphide so long as the sulphide was converted into caustic soda.

The process was again patented in 1890 (Nos. 1015, 9112, 16676 and 17815) by Ellershausen, and was used by him on a considerable scale. The sodium sulphide solution is prepared of sp.gr. 1.18 without special difficulty. The sodium ferrite by heating 100 parts of crude purple ore (Fe_2O_3) with 40 parts soda ash in a reverberatory furnace, and while still hot is charged on to a coke bed, until the layer approaches 3 ft. thickness. The sulphide solution is filtered through this bed, and then through a second bed, the beds being exhausted and changed alternately and the course of the liquor altered at the same time. The filtrate is sp.gr. 1.27, it is evaporated to sp.gr. 1.55, the impurities settled out and the clarified liquor purified by nitre and evaporated to fusion.

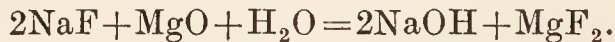
Ellershausen (Eng. Pats. 1015, 9112, 16676, 1890) first forms a ferrite of soda, similar to Löwig's (p. 230, col. 2), by heating sodium carbonate with ferric oxide; on filtering a solution of sodium sulphide through a layer of ferrite of soda, the sodium sulphide is entirely converted into sodium hydroxide, which can be easily manufactured into commercial caustic soda. The sulphur is retained in the form of an insoluble ferrosodium-sulphide, to which Ellershausen gives the formula $\text{Fe}_2\text{Na}_2\text{S}_4$, and which retains one-sixth of the total soda.

Sodium fluoride and steam



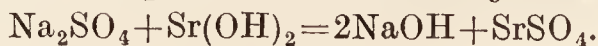
This was proposed in 1866 by Weldon (Pat. 628), the steam being superheated.

Sodium fluoride, magnesia and water



This was proposed in 1866 (Pat. 628) by Weldon, the two reagents being boiled together with water, and the solution of caustic soda formed settled and drawn off.

Sodium sulphate and strontium hydroxide

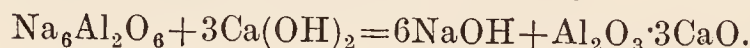


In 1868 Ungerer (Dingl. poly. J. 188, 140) dissolved sodium sulphate in water and added strontium oxide. The sodium sulphate was made from salt and ammonium sulphate by boiling the solutions, and the resulting ammonium chloride was converted by calcium carbonate into ammonium carbonate, which was utilised for converting the strontium sulphate into strontium carbonate, and this by heating was converted into strontium oxide again.

Gray (U.S. Pat. 459688) also employs the principal reaction above, but converts the strontium sulphate by magnesium carbonate into strontium carbonate, which by heating yields strontium oxide again.

Eichstadt (Pat. 15136 of 1891) also employs the principal reaction, but converts the strontium sulphate by heating with sodium sulphate and coal into a mixture of strontium and sodium sulphides, which being dissolved in hot water and cooled strontium hydroxide crystallises out; this is used over again, and the sodium hydrosulphide in the mother-liquor is used for other purposes.

Sodium aluminate and slaked lime

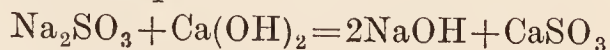


In 1874 (Eng. Pat. 2639) Grüneberg and Vorster made salt and alumina powders into a paste with water, dried, broke it into pieces and treated it with red-hot steam; hydrochloric acid escaped and sodium aluminate remains, which was dissolved and treated with lime to obtain a solution of caustic soda. The ignition vessels, however, would not stand.

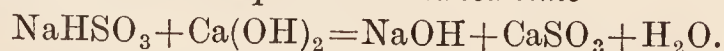
In 1877 Löwig Bros. (D. R. PP. 93 and 1650) decomposed a solution of sodium aluminate with sufficient slaked lime to precipitate all the alumina in the form of calcium aluminate which is quite insoluble, and the caustic soda solution is decanted and filtered off. According to the latter patent, the sodium aluminate is prepared by heating sodium carbonate with either bauxite or with cryolite.

In 1887 (Eng. Pat. 11492) Kayser, Williams and Young prepared an acid silico sodium aluminate by heating salt with clay in a cupola with fire gases and steam to a red heat for 24 hours; hydrochloric acid escapes and the residue, though it contains 33 p.c. Na_2O , is nearly insoluble in water. The remainder of the process is best described by Pat. 10202 of 1891 (see J. Soc. Chem. Ind. 1892, 36). The silico sodium aluminate is ground with either (1) enough soda ash to bring the total Na_2O contents to 40–42 p.c. and again ignited, which entirely alters its properties. The material is broken and treated with milk of lime to obtain caustic soda; or (2) lime or calcium carbonate and again ignited to yield insoluble calcium silico aluminate, and soluble sodium aluminate, which is dissolved out and treated with milk of lime to obtain caustic soda.

Sodium sulphite and slaked lime



and *Sodium bisulphite and slaked lime*

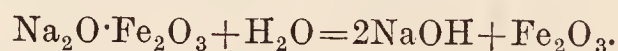


This process was first described in 1877 (U.S. Pat. 198293).

In 1879 (Pat. 4122) and also in Dingl.

poly. J. 236, 148, Gutzkow describes these processes; sulphur dioxide is absorbed by slaked lime to form calcium bisulphite solution, which by addition of sodium sulphate is converted into insoluble calcium sulphate and sodium bisulphite solution, which is boiled to form sulphur dioxide and sodium sulphite, or as this decomposition is very slow the sodium bisulphite is at once treated with an increased amount of slaked lime.

Sodium ferrite and water (hot)



In 1882 Löwig obtained D. R. P. 21593, and Eng. Pat. 4364 (J. Soc. Chem. Ind. 1883, 280) for this process.

In J. Soc. Chem. Ind. 1887, 438, an amended Eng. Pat. 4364 of 1882 was reviewed. Sodium carbonate in solution or soda ash are mixed with ferric oxide, which may be roasted iron pyrites in the form of a granulated powder. The mixture is heated in a reverberatory furnace at the cooler end at a cherry heat for three-quarters of an hour, when it is transferred to the hotter end for finishing. The finished sodium ferrite is a dark, greenish granulated mass $\text{Na}_2\text{CO}_3 + \text{Fe}_2\text{O}_3 = \text{Na}_2\text{O} \cdot \text{Fe}_2\text{O}_3 + \text{CO}_2$. It is placed on a filter bed of ferric oxide granules, where it is treated with cold water to dissolve out undecomposed sodium carbonate and the impurities of the soda, namely, sulphates, chlorides, &c. The purified sodium ferrite is then treated with water at 70°–80°, which decomposes it in half an hour and gives a pure caustic liquor of 64°–76°Tw., and after this has filtered through the filter bed, the residual oxide of iron which has a red colour is washed with hot water, and is then used again for a following batch.

It was soon found that the process was not suitable for the impure Leblanc black-ash liquors, owing to the cost of the evaporation previous to the ignition, and also by reason of the too great proportion of fusible impurities which hindered the reaction.

In 1887 Löwig (D. R. P. 41990), and Mond and Hewitt (Eng. Pat. 1974), found that the Solvay ammonia soda products were especially suitable for the Löwig process, namely, either the soda ash or the original bicarbonate of soda. Either of these was mixed with the ferric oxide and heated in a rotating cylindrical furnace fired with producer gases; the agitation essentially quickens the process by removing the evolved carbon dioxide (Ber. 1888, 3, 267; and J. Soc. Chem. Ind. 1888, 122).

In 1897 (Pats. 591 and 4227) the United Alkali Co. again lay stress on the advantages of agitation (J. Soc. Chem. Ind. 1897, p. 1015).

Although the Löwig process has been adopted by some of the largest makers of caustic from ammonia soda, and although it possesses the double advantage of producing a stronger solution of caustic, and of avoiding the very serious trouble of finding an outlet, or depositing ground, for the large quantities of lime mud produced by the lime process, it is doubtful if there is much difference in cost between the Löwig and the lime processes.

Other processes for the formation and decomposition of sodium ferrite are:—

Pollacci (Chem. News, 26, 288) heats nitre with metallic iron

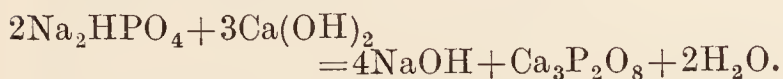


Bradburn (Eng. Pat. 6710, 1889) heated the sodium nitrate (produced as a residue in Dunlop's chlorine process) mixed with ferric oxide in a current of air to obtain the nitric acid vapours and ferrite.

Lyte (Eng. Pat. 8692, 1891) heated sodium nitrate with ferric oxide.

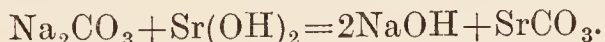
Lunge and Lyte (Eng. Pats. 13654 and 13655, 1893) evaporated sodium nitrate solution with ferric oxide to dryness and then heated in a current of mixed air and steam to obtain 95 p.c. of the nitric acid in a not too dilute solution and a residue of sodium ferrite.

Sodium phosphate and slaked lime



In 1890 (Pat. 18835) Simpson treated a solution of sodium phosphate of sp.gr. 1.13 by the above reaction. He prepared the sodium phosphate by dissolving calcium phosphate in hydrochloric acid of sp.gr. 1.05, adding sodium sulphate or bisulphate, filtering off the precipitated gypsum, evaporating the solution and finally heating to fusion, thus recovering the hydrochloric acid, dissolving the fused mass in hot water and crystallising the sodium phosphate. The calcium phosphate filtered from the caustic soda solution was used over again.

Sodium carbonate and strontium hydroxide



In 1898 Bacon (D. R. P. 99344; see Fischer's Jahresbericht der Chem. Tech. 1898, 336) proposed to treat a strong hot solution of strontium hydroxide with either a concentrated solution of sodium carbonate or even with solid sodium carbonate. The decomposition is almost instantaneous; the crystalline strontium carbonate is filtered off. Still stronger caustic soda solutions may be obtained by dissolving strontium hydrate in them and adding more sodium carbonate. The low cost of evaporating such strong caustic soda solutions is the main object of the patent. The strontium carbonate is ignited, the strontium oxide dissolved, and the strontium hydroxide crystallised. The process, however, has not been adopted, as far as is known, on the large scale.

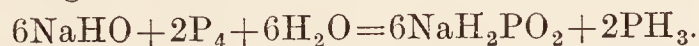
Thermal analysis of mixtures of alkali hydroxides and haloids, see Scarpa (Chem. Soc. Abstr. 1915, ii. 633).

Sodium hypochlorite NaOCl . See Vol. II. pp. 209–210. See also M. Percival Appleby (Chem. Soc. Trans. 1919, 1106).

For the catalytic decomposition of sodium hypochlorite by cobalt peroxide, see Howell (Proc. Roy. Soc. 1923, A. 104, 134). The formation and decomposition of sodium hypochlorite, see Giordani (Chem. Soc. Abstr. 1920, ii. 488). Preparation of sodium hypochlorite from the hydroxide, see Cattania and Ranucci (Chem. Soc. Abstr. 1915, ii. 344). The electrolytic preparation of sodium hypochlorite, see Paul Prausnitz (Zeitsch. Elektrochem. 1912, 18, 1025; Chem. Soc. Abstr. 1913, ii. 49, 825). Stabilisation of dilute sodium hypochlorite solutions, see Cullen and Hubbard (J. Biol. Chem. 1919, 37,

511); see also Cullen and Hubbard (J. Biol. Chem. 1919, 37, 519) for the electrolytic preparation of dilute sodium hypochlorite solutions (Chem. Soc. Abstr. 1919, ii. 231). For the stability of Dakin's sodium hypochlorite solution, see Wischo and Freiburger (Chem. Soc. Abstr. 1918, ii. 198). For the end points of indicators in dilute solutions of sodium hypochlorite, see Cullen and Austen (J. Biol. Chem. 1918, 34, 553; Chem. Soc. Abstr. 1918, ii. 265). Alteration in concentrated solutions of sodium hypochlorite, see Bouvet (Chem. Soc. Abstr. 1918, ii. 397). For the photokinetics of sodium hypochlorite solutions, see Spencer (Chem. Soc. Trans. 1914, 2565, P. 240). For the red coloration of sodium hypochlorite solutions, see Tealdi Mario (Chem. Soc. Abstr. 1922, ii. 457).

Sodium hypophosphite NaH_2PO_2 may be prepared by boiling aqueous or alcoholic soda with phosphorus until evolution of phosphoretted hydrogen ceases

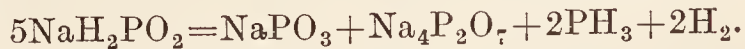


The solution is poured off, treated with sodium bicarbonate to convert any unchanged soda into carbonate, and is evaporated and digested with absolute alcohol, which dissolves the hypophosphite only. The salt crystallises out on cooling.

For pharmaceutical purposes it is usually prepared by double decomposition between solutions of sodium carbonate and calcium or barium hypophosphite (*v. Phosphorus oxides and Oxyacids*, art. PHOSPHORUS). The filtered solution is evaporated on the water-bath with frequent stirring as the mass becomes syrupy, in order to form a granular salt. To obtain the salt free from phosphite, Raymond (Pharm. J. [iii.] 10, 407) treats 25 grms. of the commercial salt with 1 gm. of barium hypophosphite in solution, and dilutes to 50 c.c., adding 200 c.c. of strong alcohol after a time. The liquid is allowed to stand and filtered from the precipitated barium phosphite and hypophosphite, and the last traces of barium having been removed by careful addition of sulphuric acid, is filtered and mixed with 500 c.c. of strong alcohol and a sufficiency of ether. The pure hypophosphite which separates is dried in a current of air.

Sodium hypophosphite crystallises in small, pearly, rectangular, very deliquescent plates containing 1 molecule of water of crystallisation. It dissolves at 15° in 1 part of water, and at 100° in 0.12 part. It is also soluble in alcohol. The aqueous solution absorbs oxygen from the air with formation of phosphite (Wurtz, Ann. Chim. [iii.] 7, 37).

When heated to 200° the crystals become anhydrous, and on further heating are converted into metaphosphate and pyrophosphate, with evolution of hydrogen and spontaneously inflammable phosphoretted hydrogen:



It explodes when triturated or heated with an oxidising agent, and has been known to explode during evaporation on the water-bath (Amer. J. Pharm. 1860, 87).

Sodium hypophosphite is a powerful reducing agent, and precipitates gold and silver from solution. With copper salts it gives a red precipitate of copper hydride Cu_2H_2 . It is used medicinally.

Sodium hyposulphite. This name is used for two substances: (1) $\text{Na}_2\text{S}_2\text{O}_3$ is now called sodium thiosulphate, is a very easily prepared compound used by bleachers and photographers. See under *Sodium thiosulphate* (p. 260). (2) $\text{Na}_2\text{S}_2\text{O}_4$, called sodium hyposulphite or commercially miscalled hydrosulphite, is a powerful reducing agent in aqueous solution used by dyers, bleachers, and sugar refiners. A full description is given by Jellinck, 1912, in Vols. 17 and 18 of *Sammlung Chem. u. chem. technischer Vorträge*.

The most satisfactory laboratory method for the production of *sodium hydrosulphite* is by the action of sodium bisulphite on *sodium formaldehyde-sulphoxylate*, which may be prepared by the reduction of commercial hydrosulphite with zinc-dust and zinc oxide in presence of formalin, and recrystallising the crystals first obtained from water at a temperature not exceeding 70°C . The purity of the product may best be determined by direct titration of a hot solution with standard methylene blue solution. Sodium formaldehyde-sulphoxylate is soluble in glycerin to the extent of about 74 grms. in 100 c.c. It has apparently no toxic action on rats when administered by intravenous injection. It was not found possible to prepare analytically pure anhydrous sodium hydrosulphite even by the method from sodium formaldehyde-sulphoxylate indicated above and salting out the product by means of strong brine, although 97.7 p.c. purity is claimed in U.S. Pat. 990457 (Eng. Pat. 11906 of 1910; J. 1911, 621). The best results obtained were yields of 55–60 p.c. of the theory with a purity of 80–85 p.c., and neither by recrystallisation nor salting out from air-free aqueous solutions in an inert atmosphere could the salt be further purified. Both sodium hydrosulphite and its products of decomposition injected intravenously into rats are toxic in doses of about 200 mgs. per kg. of body weight upwards (F. W. Heyl and F. E. Greer, *Amer. J. Pharm.* 1922, 94, 80–92; *J. Soc. Chem. Ind. Abs.* 41, 1922, p. 214; *Chem. Soc. Abstr.* 1922, ii. 288). For the formation and decomposition of sodium hyposulphite in solution, see K. and E. Jellinek (*Zeitsch. physikal. Chem.* 1919, 93, 325; *Chem. Soc. Abstr.* 1919, ii. 321). For the action of hydrogen sulphide on sodium hyposulphite, see Sinnatt (*J. Soc. Dyers*, 1914, 30, 189; *Chem. Soc. Abstr.* 1914, ii. 460).

For a method of analysing sodium hydrosulphite, see S. H. Wilkes (*J. Soc. Chem. Ind.* 42, 1923, p. 356 T). Determination of sodium hyposulphite, see also Smith (*J. Amer. Chem. Soc.* 1921, 43, 1307) and Helwig (*Amer. Dyestuff Reporter*, 1920, 7, ii. 12; *Chem. Soc. Abstr.* 1921, ii. 652, 653).

Sodium iodate NaIO_3 . Occurs native in Chile saltpetre NaNO_3 and serves as one of the principal sources of iodine. See under *Iodine*; also under *Sodium nitrate* (p. 238). Sp.gr. 4.277. For the method of determining iodate in Chile saltpetre, see *J. Soc. Chem. Ind.* 1900, 277.

Sodium iodide NaI . This salt can be prepared in a manner analogous to that given under sodium bromide (see p. 194), or by double decomposition between solutions of ferrous iodide (prepared by acting on iron filings with iodine in the presence of water) and caustic soda. It separates from solutions at temperatures

above 65° in anhydrous cubical crystals. It melts at about 650° (see Landolt Bornstein, 4th ed. 222). The sp.gr. is 3.665. The salt is very soluble in water, 100 parts of this liquid dissolving at

0°	10°	20°	30°	40°	50°	60°	80°	100°
159	169	179	190	205	228	257	295	302

parts of sodium iodide (De Coppet, *Ann. Chim.* 1883, 30, 420). For the sp.gr. of the solutions of various strengths, see Landolt Bornstein, 4th ed. 256. The boiling-point of the saturated solution is 141° . One part of the salt dissolves in 1.7 parts of ethyl or 1.2 parts of methyl alcohol at ordinary temperatures, and it is also very soluble in acetone. If sodium iodide be kept fused for a considerable time in contact with air, it loses a little iodine. Heated with carbon in presence of air it is almost completely converted into carbonate. For the electrical conductivity of sodium iodide solutions, see Kohlrausch and Holborn (*Leitvermögen der Elektrolyte*, Leipzig, 1898). The electrolytic dissociation of sodium iodide, see Holmberg (*Chem. Zentr.* 1919, i. 211; *Chem. Soc. Abstr.* 1919, ii. 283). The electrochemistry of sodium iodide in acetone, see McBain and Coleman (*Trans. Faraday Soc.* 1919, 15, 27; *Chem. Soc. Abstr.* 1920, ii. 150). The conductivity of sodium iodide in alcoholic solution, see Keyes and Winninghoff (*J. Amer. Chem. Soc.* 1916, 38, 1178; *Chem. Soc. Abstr.* 1916, ii. 407). See also conductivity on amyl alcohol, Krause and Bishop (*J. Amer. Chem. Soc.* 1922, 44, 2206; *Chem. Soc. Abstr.* 1922, ii. 813). For the electrical conductivity of solutions of sodium iodide in mixtures of ethyl alcohol and water, see Wightman and Davis, Holmes and Jones (*J. Chim. Phys.* 1914, 12, 385; *Chem. Soc. Abstr.* 1914, ii. 714). For the melting-points of mixture of KI and NaI , see Kurnakow and Shemtshushni (*Chem. Zentr.* 1907, i. 527). Sodium iodide, like sodium bromide, is used to a small extent in medicine in place of the potassium salt. See also Vol. III. p. 652. For the action of sodium iodate on acetone, see Shipsey and Werner (*Chem. Soc. Trans.* 1913, 1255, P. 117, 194).

The following hydrates are known: $\text{NaI} \cdot 2\text{H}_2\text{O}$ crystallising from solutions between 0° and $+65^\circ$; $\text{NaI} \cdot 5\text{H}_2\text{O}$ by crystallising at -14° , Panfiloff (*J. Russ. Chem. Soc.* 25, 272).

A compound $\text{NaI}_{5/2}(\text{C}_6\text{H}_5\text{NO}_2)$ has been isolated by Dawson and Goodson (*Chem. Soc. Trans.* 1904, 85, 796) from a solution of sodium iodide in nitrobenzene saturated with iodine, in the form of greenish metallic crystals which deliquesce in the air. For the compound of dextrose with sodium iodide, see Wülfing (*D. R. P.* 312643; *Chem. Zentr.* 1919, iv. 147; *Chem. Soc. Abstr.* 1919, A. 1, 574). The velocity of reaction of hydrogen peroxide with sodium iodide, see Bohnson (*J. Physical Chem.* 1920, 24, 677; *Chem. Soc. Abstr.* 1921, ii. 185). For the affinity of the reaction of potassium chlorate with sodium iodide, see Güntelberg (*Chem. Soc. Abstr.* 1916, ii. 15).

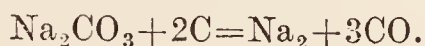
Sodium lithium iridochlorides. See Delépine (*Compt. rend.* 1914, 158, 1276; *Chem. Soc. Abstr.* 1914, ii. 461).

Sodium manganate Na_2MnO_4 . See under *Manganese* (Vol. IV. p. 216); for use as a steriliser, see Vol. II. p. 544.

Sodium metal. A short account of the history and earlier methods for the preparation of metallic sodium has been given under POTASSIUM.

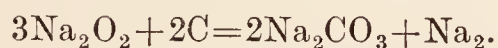
Sodium was discovered by Davy in October, 1807. He employed a battery composed of 100 plates of zinc and copper each 6 inches square, and sometimes also an additional 150 plates of 4 inches square. The piece of caustic soda employed was only 15 to 20 grains in weight, and the decomposition could only be attained by employing electricity as the common agent for fusion and decomposition. The apparent difficulties expressed by Davy probably prevented his method from receiving the attention it deserved to convert it from a philosophical experiment to a process of applied chemistry.

The first impulse to the preparation of sodium on a manufacturing scale was given in 1854 by Deville (*De l'Aluminium*, Paris, 1859, 60, 120; *Ann. Chim.* 1856, [iii.] 46, 415; *Dingl. poly. J.* 134, 369; 141, 303), who employed it to replace potassium in the manufacture of aluminium. He obtained it by mixing sodium carbonate, coal, and chalk or lime, heating to expel any moisture, recharging into wrought-iron retorts, setting these in a furnace and heating to a white heat. The reaction is



Sodium distilled over, and was collected in flat receivers of peculiar shape, designed so as to offer a large condensing surface and by rapid cooling of the vapour prevent the formation of explosive compounds of the metal and carbon monoxide, although the liability to the formation of these bodies is much less than in the case of potassium. Only about one-third of the theoretical yield of sodium could be obtained, and the method was further very costly, as small vessels only could be used (to get the necessary heat to the charge), as an excessive amount of fuel was used, and as the retorts burnt out very quickly. This process was carried out at La Glacière, Nanterre, and Salindres for upwards of 30 years; and also by the Magnesium Metal Co. at Patricroft, and the metal cost 14s. per pound retail.

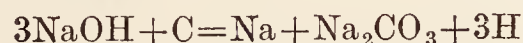
A curious laboratory experiment, described in 1898 by Bamberger (*Ber.* 451) as a lecture experiment, is to mix a few grams of sodium peroxide with coke, place in a covered crucible and heat to 300°–400°. A violent reaction occurs with great evolution of heat, and metallic sodium condenses on the upper part of the crucible and on the lid.



The reaction thus spontaneously ends where Deville's reaction began, with laborious temperature elevation and heat absorption.

A much better process was that devised by Castner in 1886 (*Eng. Pat.* 7395, 1886; see *J. Soc. Chem. Ind.* 1886, 538, 601). The starting-point was molten caustic soda, and the reducing agent was obtained by adding finely divided iron to melted pitch and coking the mixture in cylinders; the result is an intimate mixture of carbon and iron. The process was conducted in large iron crucibles mechanically placed in contact with its cover and vapour delivery pipe held in the gas furnace; distilla-

tion of the sodium took place at 1000°C. The patent gives a complicated reaction in which the whole of the soda is converted into sodium, but according to H. Becker (*Die Elektrometallurgie der Alkalimetalle-Monographien ü. Angewandte Elektrochemie IX. Band* 1903, 2) the reaction was



so that only one-third of the sodium was obtained, and the iron took no part in the reaction. This process was worked on the large scale for some time by the Aluminium Co. at Oldbury, and effected a considerable reduction in the price of sodium. See also Schnabel's *Metallurgie*, 2nd ed. 2, 836.

The caustic soda carbon process was improved by Netto (*Eng. Pats.* 14602, 1887, and 17412, 1887; see *J. Soc. Chem. Ind.* 1888, 851; 1889, 122; and *Eng. & Min. Journ.* 45, 449) by charging coke into vertical iron retorts and

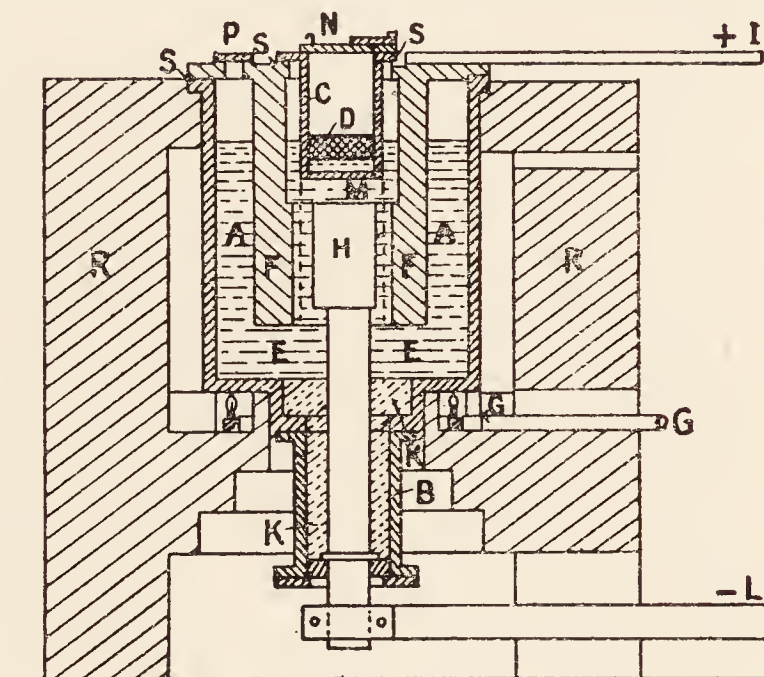


FIG. 50.

running in a slow stream of molten caustic soda at the top through a luted pipe and running out through another luted pipe at the bottom of the retort the resultant molten sodium carbonate. The sodium vapour and hydrogen were led away by a side pipe to the condensers, and the coke could be replenished from time to time through a suitably closed opening. The sodium is produced at a lower temperature and more regularly than when the sodium carbonate is not removed. The process was operated by the Alliance Aluminium Company at Wallsend, near Newcastle.

Both the above processes were succeeded by Castner's caustic soda electrolytic process (*Eng. Pat.* 13356, 1890; see *J. Soc. Chem. Ind.* 1891, 777), which obviated many of the difficulties met with in the older purely chemical processes, as it requires a very much lower temperature, and enabled sodium to be produced in large quantities at a relatively small cost. At the present time the whole of the sodium of commerce is manufactured electrolytically.

The electrolytic apparatus employed by Castner is shown in the accompanying diagram (Fig. 50). It consists of an iron vessel A, mounted in brickwork R, in which the caustic soda is melted by means of the gas burners G. The vessel A is provided with an extension pipe B,

through which the metallic negative electrode H passes, the intervening space K being filled with molten caustic which solidifies and seals H in position. Immediately above this electrode is fixed a tubular iron receptacle c, fitted with a lid, N, and having a cylindrical piece of wire gauze attached to its lower end. This gauze is placed intermediate between the faces of H and F, and is indicated in the figure by dotted lines. P is an opening for the escape of oxygen gas and for the feeding of more molten caustic soda, and S is an insulating medium such as asbestos. The current is supplied through the conductors I and L. On passing the current the fused caustic soda is decomposed, and the liberated sodium D, being specifically lighter than the electrolyte, rises to the surface of the caustic in c, whence it is removed from time to time by a perforated iron spoon which allows the molten caustic to drain through while retaining the metal. Fresh caustic soda is added to the bath from time to time, thus rendering the process continuous. In order to secure a fair yield of the metal for the current applied it is necessary that the temperature of the electrolyte should not rise more than 20° above the melting-point of the alkali, *i.e.* should not exceed 330° . Any increase of temperature is followed by a proportionate loss of product and waste of energy; it is possible to adjust the electrical current so that the proper temperature will be maintained in a previously melted bath without applying external heat. A current of 1000–1200 ampères with an E.M.F. of 4–5 volts is usually employed. Oxygen is evolved at the anode, and sodium and hydrogen are evolved at the cathodes, and according to the equation $2\text{NaOH}=\text{Na}_2+\text{H}_2+\text{O}_2$ a yield of 80 p.c. is obtained on the amount of current employed. Slight but harmless explosions of the hydrogen and oxygen formed sometimes take place.

The Castner process is worked in England at Wallsend-on-Tyne by the Castner Kellner Alkali Co., and in Germany by the Farbwerke von Meister, Lucius & Brüning at Höchst am Main, and by the Elektrochemischen Werke Natrium at Rheinfelden. It is also operated by the Compagnie d'Electrochimie at Gavet in France, and by the Electrochemical Co. at Niagara Falls, U.S.A.

According to Smith and Veazey (U.S. Pat. 1375330) the above apparatus may be used with a different electrolyte, *viz.* a mixture of Na_2CO_3 43.5; NaCl 23.2; and KCl 33.3 p.c.; the mixture melts at 565° .

Another form of cell to avoid the volatilisation of the sodium is referred to in J. Soc. Chem. Ind. 1914, 600, and 1916, 1068; *see also* J. Soc. Chem. Ind. 1915, 967, and 1916, 111.

Another apparatus for the production of sodium by the electrolysis of fused caustic soda is that of Rathenau and Suter, which is used by the Elektrochemischen Werke, Bitterfeld, Germany. The negative electrodes are allowed just to touch the surface of the molten electrolyte contained in the iron vessel (Fig. 51). The surface tension causes the electrolyte to rise up slightly, so that the electrodes are not actually below the surface of the molten caustic, and the metallic sodium produced at the ends of the electrodes is protected from the heat generated

by the passage of the current through the electrolyte; it is removed by perforated ladles as in the Castner process. The current density in this process must not exceed 10 ampères per sq. cm. of cathode surface.

A slightly different apparatus is that of Becker (Eng. Pat. 11678, 1899), worked by the Usines de Rioupéroux in France, a mixture of sodium carbonate and caustic soda being

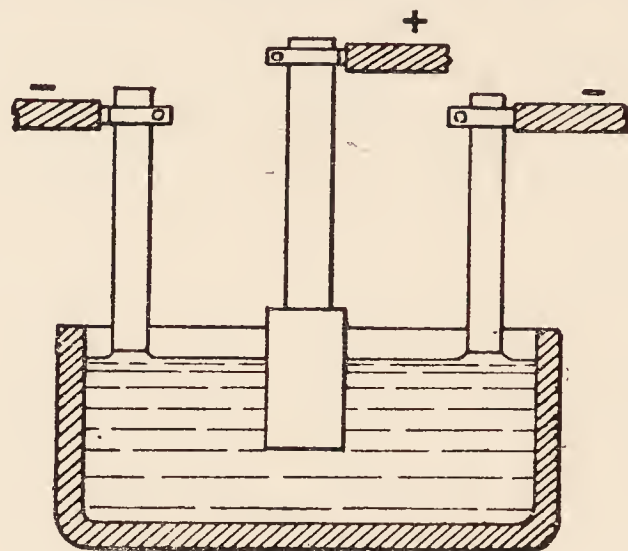


FIG. 51.

electrolysed in the decomposition cell shown in the following diagram (Fig. 52). The cathode B is cone-shaped, and the sodium as it is produced rises to the collecting hood d, made of iron or ferronickel, and connected to the negative electrode through a resistance, so that when the metallic sodium comes into contact with the sides of the hood it is in electrical connection

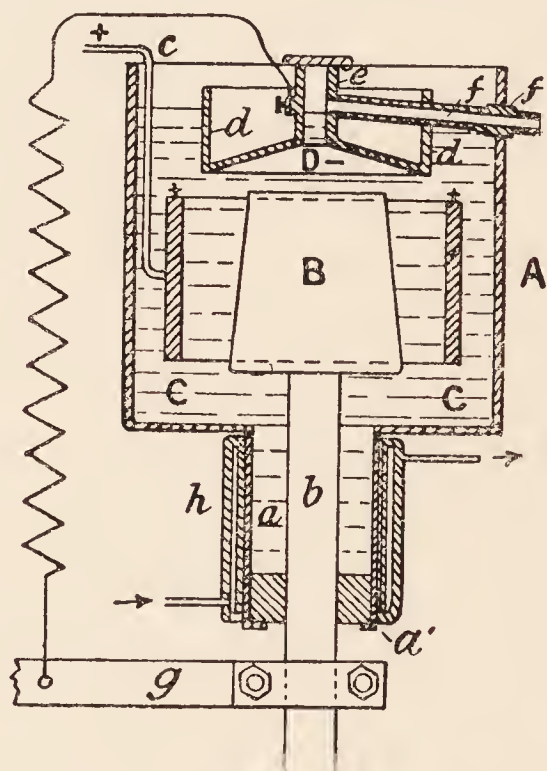


FIG. 52.

with the cathode, and is not further acted on by the molten electrolyte. The sodium being specifically lighter than the electrolyte rises in the hood and flows out through f. The hood d is cooled either by water or simply by a current of air circulating round it. The process is described and photographed by H. Becker in Monographien über Angewandte Elektrochemie—die Elektrometallurgie der Alkalimetalle, 1903, 52–58.

The process of Darling (Eng. Pat. 5808, 1894), which was worked at Philadelphia, U.S.A.,

differs from the preceding ones in that the electrolyte in part consists of fused sodium nitrate. As sodium reacts with the nitrate to form sodium nitrite, sodium monoxide, and sodium dioxide, a divided cell was used, the anodic compartment containing fused sodium

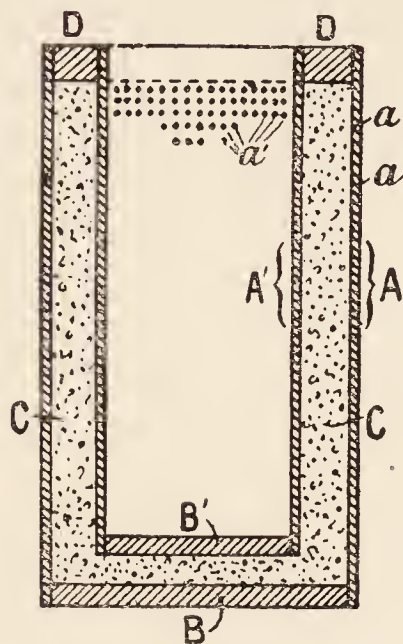


FIG. 53.

nitrate, while the electrolyte in the cathode compartment consisted of fused caustic soda. The Na cations are liberated at the cathode, and the NO_3 anions split up at the anode into NO_2 and O , which are passed into water and oxidised to form nitric acid.

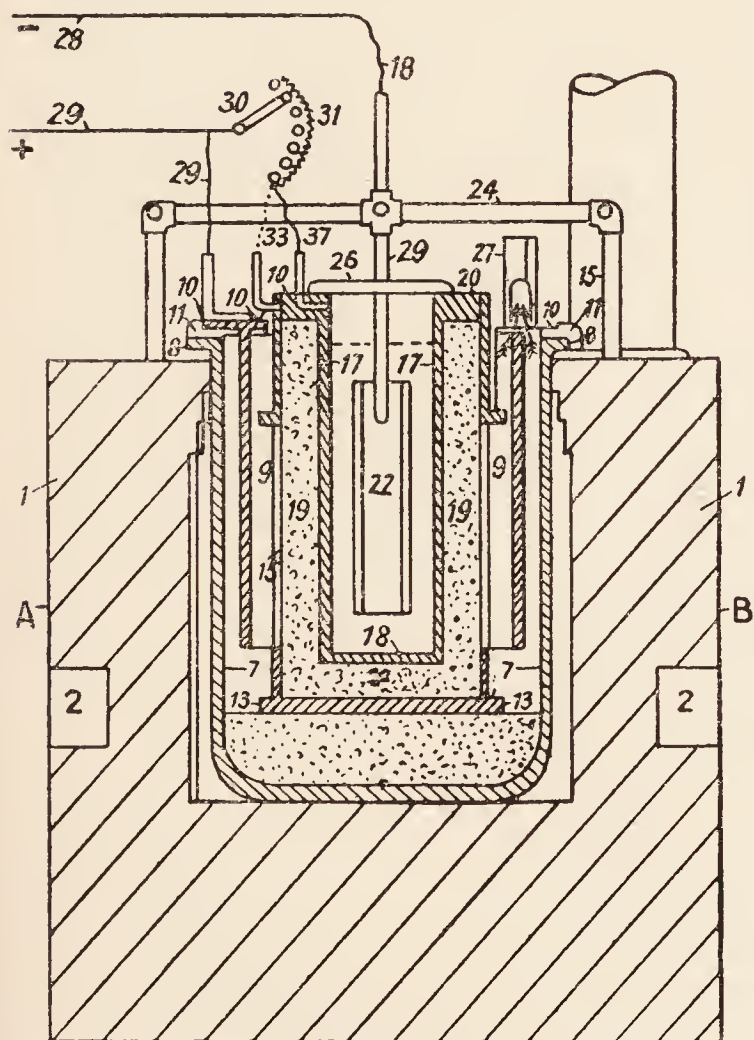


FIG. 53A.

The apparatus is depicted in Fig. 53 and Fig. 53A. The cathode compartment (parts 17, 18, 19, 20), Fig. 53A, consisted of a double casing made of perforated sheet iron, the intervening space being filled with a mixture of Portland cement and magnesia, Fig. 53. The cathode compartment stood inside the iron

cell (7), the bottom of which was covered to a depth of 6 ins. with Portland cement, upon which the cathode cell rested. The iron outer cell (7) was connected with the positive source of current, and its bare interior surface formed the acting anode. The cathode was the 4-in. iron tube (22). About 5 p.c. of the total current was allowed to pass through the metal diaphragm (17) by means of a regulating resistance (31), and although this caused a waste of energy it greatly prolonged the life of the cell. The nitrous gases were led away by the pipe (27). At the commencement of the electrolysis the charge must be melted by applying external heat. Fresh charges of sodium nitrate are introduced into the anodic compartment from time to time, and the sodium and a not inconsiderable portion of the cathode electrolyte were removed periodically by a ladle. The process was capable of being run 18 days, when the diaphragms had to be removed and renewed. Twelve such cells were worked together, each one taking 400 ampères at 15 volts. The efficiency was about 50 p.c. and the difficulties were so numerous that the process was abandoned (Haber, *Zeit. f. Elektrochemie*, 9, 369); but according to *J. Soc. Chem. Ind.* 1916, 111, the process is good.

Many attempts have been made to employ the cheaper sodium chloride as an electrolyte in the production of metallic sodium, but with only partial success. The chief drawbacks lie in the high temperature necessary to fuse the salt, and that at this temperature the liberated sodium unites with sodium chloride to form sodium subchloride, which either undergoes oxidation at the surface of the mass, or unites with the chlorine set free at the anode to reform the original NaCl . The intense activity of the liberated chlorine is a further objection to the process. According to *J. Soc. Chem. Ind.* 1916, 690, zirconia resists all attack under these conditions.

Attempts have been made to improve the process by lowering the fusing-point of the electrolyte by the addition of various salts, the most successful being that of Grabau (D. R. P. 56230, 1891; Eng. Pat. 16060, 1890), whose process was formerly worked commercially; the added salts consisted of a mixture of potassium chloride and strontium chloride. This electrolyte melted below a red heat, and at the most suitable temperature a current efficiency of 97 p.c. was obtained, but the metal produced contained 3 p.c. of potassium (*Monographien ü. Angewandte Elektrochemie*, 22, 10). The addition of sodium fluoride has also been tried (*Konsort. für Elektrochemie Nürnberg*, D. R. P. 160540, 1904).

A list of other patents relating to the manufacture of metallic sodium, together with an indication of the improvements claimed, is given below:—

J. Dickson, Eng. Pat. 2266, 1862 (electrolysis of the fused chloride); E. Sonstadt, Eng. Pat. 1763, 1863 (replacement of the chalk or lime in the ordinary process by gypsum); J. Anderson, Eng. Pats. 2801, 1867; 2134, 2216, 3493, 1871; 513, 1089, 1872 (heating the slag obtained by the action of hot air or steam on strongly-heated minerals containing silicates of sodium or potassium with carbon in a current of highly

heated carbon monoxide); H. Larkin and W. White, Eng. Pats. 1990 and 3505, 1869; 23, 1871 (modification of the distillation process); W. Clark, Eng. Pat. 473, 1875 (electrolysis by a specially arranged current); W. Anderson Smith, Eng. Pat. 363, 1876 (use of a mixture of soda or potash with pitch, also a modified retort and condenser); W. P. Thompson, Eng. Pat. 2101, 1879 (decomposition of the hydroxide by fluid iron in a Bessemer converter); C. A. Faure, Eng. Pat. 6058, 1882; and 5489, 1883 (heating the alkaline compound in hydrogen or nitrogen by an electric current); A. L. Nolf, Eng. Pat. 4349, 1882 (electrolysis of a strong solution of sodium chloride with a mercury cathode); F. P. Harned, D. R. P. 26961, 1883 (modification of the mixture used); E. A. Höffner, D. R. P. 30377, 1884 (electrolysis of the fused chloride with a copper or silver anode); S. G. Thomas, Eng. Pat. 6367, 1884 (passage of heated water-gas through the usual mixture without applying external heat); Max Sprenger, D. R. P. 39554, 1886 (electrolysis of the chloride *in vacuo*); E. C. Kleiner-Fiertz, Eng. Pat. 8531, 1886 (electrolysis of cryolite); J. B. Thompson and W. White, Eng. Pat. 8426, 1887 (heating a coked mixture of alkaline carbonate and tar); O. M. Thowless, Eng. Pat. 12486, 1887 (use of a mixture of separately heated alkaline carbonate and coke); L. Grabau, Eng. Pat. 9904, 1887 (comprises the cooling of the cathode in electrolytic processes; the metal rises to the surface and is drawn off by a pipe); H. C. Bull, Eng. Pat. 10199, 1887 (electrolytic); A. B. Cunningham, Eng. Pat. 3601, 1888 (heating charcoal with caustic soda); G. A. Jarvis, Eng. Pat. 4842, 1888 (modification of the process for reduction by coke); W. G. Forster, Eng. Pats. 9391, 10785, and 14394, 1888 (reduction of fused alkali with coal-gas); H. M. Wallis, Eng. Pat. 12626, 1888 (modification of the mixture commonly used); W. White, Eng. Pat. 13125, 1888; H. S. Blackmore, Eng. Pat. 15156, 1888; G. M. Westman, Eng. Pat. 17736, 1888; W. White, Eng. Pat. 9784, 1889 (all relating to modifications of the mixture or distillation apparatus); T. Parker and A. E. Robinson, Eng. Pat. 11707, 1889 (electrolysis of a mixture of the hydroxide or carbonate and carbon); H. C. Bull, Eng. Pat. 10735, 1892 (electrolysis of the fused chloride in a divided cell); C. J. T. Vautin, Eng. Pat. 10197, 1894 (production of a lead-sodium alloy by the electrolysis of fused sodium chloride with a cathode of molten lead, the alloy being run off and distilled in a retort lined with magnesia or carbon); J. A. Kendall, Eng. Pat. 23045, 1895 (reduction of a mixture of carbonate or hydroxide and carbon in hydrogen gas); G. Wolfram, Eng. Pat. 18604, 1898 (distillation of a mixture of caustic soda and calcium carbide); T. Ewan, Eng. Pat. 14739, 1902 (use of a divided cell in the electrolysis of fused caustic soda); Cassel Gold Extraction Co., Fr. Pat. 330987, 1903 (modified apparatus for electrolysis); T. Parker, Eng. Pat. 19196, 1903 (calcination of a mixture of sodium aluminate and carbon in an electric furnace, sodium volatilising); J. Raschen, G. Clayton, and the United Alkali Co., Eng. Pat. 2152, 1904 (employment of sodium-lead alloy as anode in electrolysis of caustic soda); P. L. Hulin, Eng. Pats. 22824, 1908; 6063, 1910

(modified apparatus for the electrolysis of fused caustic soda); A. C. Vournasos, Eng. Pat. 23689, 1908 (preparation of sodium by heating a mixture of salt and lead shot in a special furnace); Chemische Fabrik Griesheim Elektron, Eng. Pat. 29795, 1909 (heating sodium sulphide with calcium carbide); P. A. Emanuel, U.S. Pats. 957754-957756 and 957848, 1910 (production of sodium from various sodium salts by heating with carbon); R. J. McNitt, Eng. Pat. 20519, 1910 (electrolysis of fused salt in presence of lead); E. A. Ashcroft, Eng. Pats. 12377, 1903; 5013, 1910 (electrolysis of a mixture of sodamide and caustic soda with a fused lead anode); The Nitrogen Co., Eng. Pat. 20386, 1910 (formation of an alloy of sodium with a heavy metal by electrolysis, and utilisation of this as anode for electrolysing a bath of fused alkali cyanide); P. L. Hulin (J. Ind. Eng. Chem. 1911, 130) (modified apparatus for the electrolysis of caustic soda).

Properties.—Freshly-cut sodium exhibits a silvery metallic lustre, which rapidly disappears on exposure to air with the production of a greenish phosphorescence (Linnemann, J. pr. Chem. 1858, [i.] 75, 128). For the luminescence during oxidation, see Reboul (Chem. Soc. Abstr. 1919, ii. 311). According to Long (Chem. Soc. Trans. 1861, 123) sodium crystallises in acute octahedra which belong to the quadratic system.

At a temperature of -20° sodium is hard, at 0° it becomes ductile, and at the ordinary temperature it is of a waxy consistency, and at 50° it softens considerably. For thermal dilatation, see Bernini and Cantoni (Chem. Soc. Abstr. 1915, ii. 82). According to Met. and Chem. Eng. 1915, 954, sodium is allotropic, and at 95° β Na changes into α Na, but the change is not reversible. Sodium melts at 97° (Karnakow and Puschin, Zeitsch. anorg. Chem. 1902, 30, 109); 97.9° (Rengade, Compt. rend. 1913, 156, 1897); 97.61° (Griffiths, Proc. Roy. Soc. 1914, A. 89, 561). For the latent heat of fusion, see Griffiths (Chem. Soc. Abstr. 1914, ii. 245). Sodium boils at 882.9° (760 mm.), (Heycock and Lamplough), giving a vapour which in thin layers appears colourless, but has a purple colour when viewed in quantity by transmitted light, and exhibits a green fluorescence. For heat of vaporisation, see Ladenburg and Minkowski (Chem. Soc. Abstr. 1922, ii. 194). Its absorption spectrum has been examined by Roscoe and Schuster (Proc. Roy. Soc. 1874, 22, 362), and by Wood and Moore (Phil. Mag. 1903, 6, 362), and the ultra-violet portion by Wood (*ibid.* 1909, 18, 530).

The sp.gr. of sodium has been determined by Baumhauer (Ber. 1873, 6, 665), who obtained the values 0.9735 at $13.5^{\circ}/13.5^{\circ}$ and 0.9943 at $10^{\circ}/10^{\circ}$. Later determinations by Dewar (Chem. News, 1902, 85, 289) and Richards and Brink (J. Amer. Chem. Soc. 1907, 29, 117) have afforded the values 0.9724 at $0^{\circ}/0^{\circ}$ and 0.9712 at $20^{\circ}/20^{\circ}$ respectively. Hackshill found 0.9723 at 0° and 0.9385 at 96.5° . Ramsay (Ber. 1880, 13, 2145) found the sp.gr. of fused sodium near its boiling-point to be 0.7414. At 97.6° the sp.gr. of the solid is given as 0.9519, while the liquid is 0.9287 (Landolt Bornstein, 4th ed. p. 165). Coefficient of expansion when solid 0.000216 between 0° and 80° , and when liquid 0.000274 between 100° and 180° (Hackshill, Compt. rend. 1911, 152, 259).

Specific heat (solid) $0.2811 + 0.000233t$; (liquid) 0.330 at 98° ; heat of fusion 27.21 ; ratio of atomic heat of fusion to absolute m.p. 1.69 (Rengade, *l.c.*). Cf. E. Griffiths. *l.c.*; Eastman and Rodebush, Chem. Soc. Abstr. 1918, ii. 149. At low temperatures, see Günther (Chem. Soc. Abstr. 1921, ii. 16)

No satisfactory determination of the vapour density of sodium has at present been carried out, owing to the difficulty of finding a suitable material for the construction of the apparatus capable of resisting attack by the sodium vapour (*cf.*, however, Ruff and Johannsen, Ber. 1905, 38, 3602). The molecular weight of sodium was determined by Ramsay (Chem. Soc. Trans. 1889, 55, 521) by Raoult's method. He found the molecular weight to vary between 15.1 and 21.6 according to the ratio of the metal to the solvent (mercury); but the method is open to objection on account of the existence of numerous well-defined compounds of sodium and mercury.

Sodium has been obtained in the colloidal state, forming an unstable violet solution in ether, by passing an electric current of high potential by means of aluminium poles through the granular metal contained in a porcelain dish and covered with ether (Svedborg. Ber. 1905, 38, 3616). For the chemical constants of sodium, see Ladenburg and Minkowski (Chem. Soc. Abstr. 1922, ii. 191). For the allotropy, see Cohen and Wolff (Chem. Soc. Abstr. 1915, ii. 634).

When sodium is exposed to ordinary, *i.e.* moist, air the surface is instantly tarnished and the film of hydroxide, carbonate, oxide and suboxide protects the interior bulk of the metal from further action for very long periods of time, so that it is quite unnecessary to keep it submerged in a mineral oil, and so it may be handled, weighed and packed in ordinary tin canisters or iron drums with only a very slight surface deterioration. In air or oxygen that has been dried by bubbling through a couple of gas washing tubes containing sulphuric acid, sodium at temperatures below 50° is slowly covered with a white film; at temperatures slightly above its melting-point it also slowly becomes covered with a film of greyish-white oxides, and if the gas supply is limited and the temperature be kept below 180° the final product is the monoxide Na_2O ; if, however, the temperature be allowed to go higher, then it may burn with a yellow flame and the yellow peroxide Na_2O_2 is formed; and up to 350° no higher oxide than this is produced. In air or oxygen that had been completely dried by standing a considerable time over P_2O_5 , sodium does not tarnish, whether it be solid, or molten, or heated till it volatilises, and if a deflagrating spoon containing sodium heated to burn brightly in the air is plunged into a jar of perfectly dry air the combustion is instantly extinguished; but restarts spontaneously when the spoon is again brought into ordinary air (Holt and Sims, Trans. Chem. Soc. 1894, 433).

Dry chlorine has no action on sodium, even at the melting-point of the latter (Wanklyn, Chem. News, 20, 271; Cowper, Chem. Soc. Trans. 1883, 155); neither has bromine at temperatures up to 150° , whilst sodium and iodine can be heated together to 350° – 360° without

combination (Merz and Holzmann, Ber. 22, 872). Dry hydrogen chloride can also be left in contact with sodium for many weeks without appreciable action resulting. The presence, however, of mere traces of water is sufficient to cause immediate and violent combination in all these cases. Dropped upon cold water it is buoyed up just above the surface by the disengaged hydrogen but not evolving sufficient heat to ignite the gas, finally there remains a globule of molten NaOH , and when after sufficient cooling this drops into the water it bursts into flame with explosive violence and is scattered around. If water at 60° be used, or the free motion of the metal be hindered by increasing the viscosity of the liquid by the addition of gum or starch, the evolved hydrogen ignites, burning with a characteristic yellow flame. Sodium decomposes water vapour even at -98° .

With the exception of gold, silver, and copper, sodium conducts heat and electricity better per unit area of cross section than any other metal.

Metallic sodium is largely used in the manufactures of cyanides (*see* Vol. II. CYANIDES, at p. 438), of sodamide (used in the artificial indigo industry), of sodium monoxide, and sodium peroxide, also for refining steel, for making sodium amalgam (for extracting gold from its pulverised ores), and for purifying naphthalene from sulphur compounds (J. Soc. Chem. Ind. 1921, R. 445). In the laboratory it is employed in many organic syntheses, in the preparation of pure caustic soda and in conjunction with alcohol as a powerful reducing agent.

Sodium acts on an anhydrous solution of lithium chloride in alcohol, precipitating sodium chloride and leaving in solution lithium ethoxide, which may be separated by taking advantage of its diminishing solubility with rise of temperature. Metallic sodium has also been used to reduce the anhydrous chlorides of glucinum, chromium, uranium, vanadium, and zirconium in a closed steel bomb, the metals being obtained in a fairly pure state (M. A. Hunter and A. Jones, Amer. Electrochem. Soc. 1923, 44, 35).

Sodium monoxide Na_2O is produced by the combustion of sodium in air or oxygen, using a limited supply of gas and keeping the temperature below 180° (Holt and Sims, Chem. Soc. Trans. 1894, 442). It can be obtained perfectly pure by partially oxidising the metal and separating the unchanged sodium by distillation *in vacuo* at a low temperature (Rengade, Compt. rend. 1906, 143, 1152; J. Chem. Soc. Abstr. 1907, ii. 83, and 1908, ii. 457). The monoxide is also formed when metallic sodium is heated with sodium nitrite or nitrate, nitrogen being liberated.

It is obtained, according to the Badische Anilin u. Soda Fabrik (J. Soc. Chem. Ind. 1903, 212), by firing a mixture of sodium peroxide and sodium; and also mixed with calcium oxide by gradually adding calcium nitrate to heated sodium (*ibid.* 796). The Basle Chemical Works modify the first method by adding also a small percentage of sodium hydrate and heating to 400° (*ibid.* 865).

Sodium monoxide is a white, hygroscopic substance of sp.gr. 2.27 . Heated above 400° it decomposes into the dioxide and metal.

Hydrogen at 180°–200° converts it into a mixture of hydroxide and hydride (Rengade, J. Chem. Soc. Abstr. 1907, 2, 457). It combines when heated with fluorine, iodine, and sulphur with incandescence, and reacts violently with water, forming sodium hydroxide. It dissolves in sodium, and possibly forms suboxides.

Sodium monoxide is the basic oxide of sodium, from which are derived all the sodium salts, and is the real 'soda' of the older chemists. It cannot be obtained from its hydrate 'caustic soda' by heating, and owing to the difficulties of the preparation it has only recently found application.

Sodium nitrate (*cubic nitre*; *Chile saltpetre*) NaNO_3 . This important salt occurs as *nitratine* in the natural and artificial accumulations of potassium nitrate, and in other deposits where it has been produced similarly to that salt (*v. Potassium Nitrate*, art. POTASSIUM).

For the oxidation of ammonia and nitrates by micro-organisms under different conditions, see Gawda (Soil Sci. 1924, 17, 57; Chem. Soc. Abstr. 1924, i. 818). For the reduction of sodium nitrate and potassium chlorate during the putrefaction of viscera, see Ghigliotto (Ann. Falsif. 1924, 17, 93; Chem. Soc. Abstr. 1924, 126, i. 792).

Sodium nitrate occurs in enormous quantities, admixed with only small quantities of the potassium salt, in the province of Tarapaca, 20°S. lat. in Northern Chile, and these, with the exception of certain deposits in Bolivia, are the only sources from which the salt is extracted on the large scale.

The nitrate deposits do not form beds of any definite geological character. Their origin has been the object of much speculation, but the absence of bromine from the deposits may be taken as evidence that they are not of marine origin. The nitrate belt stretches along the eastern slope of the coast range of mountains.

The nitrate belt of Tarapaca has a width of about $2\frac{1}{2}$ miles, and is included between latitudes 19°S. and 27°S. for lengths which total about 260 miles. The main belt is at 20°S. and 15–20 miles from the coast, which distance is occupied by the coast hills without any passage through them to the sea. The railway to the nitre belt starts from the port of Iquique, runs south for 10 miles rising 2000 ft., and then runs east through the coast hills for 20 miles and rising another 1000 ft. West of the coast hills and 150 ft. below the lowest passage through the coast hills lies the plain of Tamarugal, rising extremely slowly for about 45 miles towards the east to the feet of the Andes. The nitrate belt lies along the junction of this plain with the eastern feet of the coast hills, and has been formed by the nitrification of the vegetable remains in this great plain, and the removal of the nitrates and other soluble salts through the porous alluvial soil to the lowest points of this drainageless area.

The 'caliche,' as the crude nitrate is called, is never found at any great depth. It is usually covered to a depth of 6 or 10 ft. by a crust or 'costra,' consisting of a conglomerate of porphyry, felspar, magnesia, sodium chloride, &c., cemented together by gypsum, and covered by a layer of fine loose sand to a depth of 8 or 10 ins. The caliche proper forms a rock-like mass from

3 to 6 ft. deep, and varies in colour from almost pure white, through shades of yellow, orange, brown, bluish-grey, &c. The lower part of the caliche (known as 'congeló') contains but little nitrate, and abounds in the chlorides of sodium and magnesium, and in sulphates. It lies upon a pale, yellowish-brown, loose clay free from nitrate, and overlying the primitive rock.

Various qualities of caliche are worked, containing of nitrate, from 40 to 80 p.c. in the best quality, from 30 to 40 p.c. in the second, and from 17 to 30 p.c. in the inferior kinds.

The following analyses show the composition of (1) one of the largely-worked deposits (Forbes, Phil. Mag. 1866, 32, 135); (2) the deposit worked at the Oficina Ramirez (Harvey, Proc. Inst. C. E. 1885, 82, 337):—

	(1)	(2)
Sodium nitrate .	21·01	51
Sodium chloride .	55·27	26
Sodium sulphate .	4·74	6
Calcium chloride .	0·33	—
Potassium iodide .	0·87	—
Aluminium sulphate .	9·81	—
Magnesium sulphate .	5·93	3
Insoluble matter .	2·04	14
Moisture .	—	—
	100·00	100

Other soluble salts are also present as sodium iodate, which is periodically and partly extracted, sodium chlorate and perchlorate, all of which are deleterious to the product.

A good ground would contain a bed 3–4 ft. thick, containing 40–45 p.c. NaNO_3 . The upper overlayer varies from 4 to 20 p.c. In poor grounds, however, 20 p.c. nitrate would become 'caliche.' The ground is broken by blasting and the big blocks divided into smaller ones with crowbars and the lumps of 'caliche' separated from the overlayer or 'costra' by hand.

The Tarapaca deposits were worked as early as 1813 by the Spaniards, who exported 23,732 quintals (of 100 pounds) in that year; but the industry was but little developed until 1852, when small refining works were established by Smith and Sandes.

The method of separating the nitrate from the caliche consists merely of lixiviation. At the Oficina of Ramirez (Tarapaca) the caliche is crushed roughly into 2-in. lumps. The tanks are 32 ft. long by 9 ft. deep by 6 ft. wide, and contain (1) a steam-pipe coil 5 ins. diameter, which makes the circuit of the tank five times, and is arranged in tiers about 9 ins. from the sides, (2) a false bottom about 1 ft. from the real bottom of the tank. The tanks are built in a series of six, connected by a 9-in. pipe for passing the liquor from one to the other. The 'caliche' is charged on to the false bottom in each tank, and water is fed into one of the tanks and through it into the others all down the series, so that after due time the first tank contains exhausted caliche while the last tank delivers liquor (at 112°C. with about 80 lbs. nitre to the cubic foot) into the crystalliser tanks. After cooling for 4 or 5 days in the crystallisers so much nitre has crystallised out that the strength of the liquor is reduced to about 40 lbs. nitre per cubic foot. This mother-liquor is used in the systematic lixiviation of the 'caliche' described above, by adding it to the weak liquor

from final exhaustion of the 'caliche,' as that flows into the next following tank.

A good form of crystalliser is a sheet-iron tank 25 ft. by 18 ft. by 2 ft. 9 ins. to 3 ft. deep, with an inclined bottom to assist in the draining of the crystals. Six such lixiviating tanks as have been described require about 44 of these crystallising vessels.

The nitrate from the crystallisers is drained and is placed on the drying floor to dry for 5 or more days, when its composition is as follows:—

	First quality	Second quality
NaNO ₃ . . .	96.5	95.2
NaCl . . .	0.75	2.5
Na ₂ SO ₄ . . .	0.45	0.6
H ₂ O . . .	2.3	1.7

The fuel consumption averages about 1 ton coal to 7 tons nitrate produced.

For further details of the nitrate manufacture, see paper by Newton, J. Soc. Chem. Ind. 1900, 408, from which most of the above statements have been taken.

The account given by Diaz-Ossa, abstracted into J. Soc. Chem. Ind. 1912, 31, 771, gives a little more chemical information, and describes the caliche as containing 35 p.c. sodium nitrate.

A still more detailed account is given by Hobsbaum and Grigioni in J. Soc. Chem. Ind. 1917, 52–63, from which the following is taken. A works with all mechanical improvements in 1911 was treating caliche containing 25 p.c. sodium nitrate, and 56.4 p.c. only of the nitre in the caliche was converted into commercial form. The most modern methods which are described in fair detail also leave nearly 50 p.c. of all the original nitrate in the residue thrown out of the last lixiviating tank. From 1912, with the necessity of working still poorer caliches, viz. 20–17 p.c. nitre and even less, there have been serious attempts to remodel the old wasteful rough styles of working.

(1) Butler crushes the caliche as before, but then sifts it through a 6 mm. mesh. The treatment is begun on the fines by grinding in ball mills with liquor of 150 grms. nitre per litre, heating the mill and grinding until the liquor tests 75°Tw. at 80° and 450 grms. nitre per litre; the slurry is filtered, the cakes washed with saturated NaCl brine, and are then discharged with only 0.25 p.c. of nitre; the strong liquor obtained is then used to extract the coarse crushings by the old method. This method was able to treat caliche containing only 14.5 p.c. nitre.

(2) Gibbs' method was to work caliche with only 10 p.c. of salts. The caliche, without the hitherto customary hand picking, was broken to only 2–3 ins. size, and coarse and fine charged into a rotating mill without balls, and into which a weak nitre solution at 50°C. is also fed continuously. The hard caliche is thus disintegrated by the removal of the soluble binding salts, without undue breaking or grinding of the insoluble stones, sand, &c. The pulp passes continuously on to, say, four-ore classifiers, where the dissolving of the soluble matters continues until completed, so that clean sand, gravel, stones, &c., are discharged containing not more than 0.25 p.c. of nitre, and the turbid liquors carrying the insoluble portions that pass an 80-mesh sieve, and which are very small in

amount, pass to an Oliver continuous vacuum filter where the insoluble matters are removed, washed, and thrown out and the filtrate discharged containing per litre 450 grms. NaNO₃, say 200 grms. NaCl, and 50–60 grms. MgSO₄, MgCl₂, Na₂SO₄, &c. This liquor is then evaporated first in a double effect vacuum evaporator, and then in a single effect salting out evaporator at atmospheric pressure till its boiling-point reaches 124°C., by which time half the NaCl has been deposited and removed. The hot solution is run into the nitrate crystalliser, where, by applying a vacuum, the solution is further concentrated by its own sensible heat, and being thereby cooled, deposits the nitre in crystals, while the accompanying NaCl remains in solution. The effect of such scientific methods upon the failing supply of the old rich caliches and upon the competition of the synthetic manufacture of nitrates has yet to be seen.

The occurrence of up to 1 p.c. of sodium iodate in the caliche has also to be considered; the work of extracting this is only intermittent; the mother-liquors are periodically treated with sodium bisulphite, which throws down iodine, the method is exceedingly crude, and when enough has been extracted to last as stock for years, no more is extracted until a fresh stock is required.

If the preparation of sodium nitrate were conducted on rational chemical lines, the yield of nitrate could be much increased, and the by-products, instead of being only small quantities of iodine, potassium perchlorate, and sodium chloride (Diaz-Ossa, J. Soc. Chem. Ind. 1912, 771, Abstr.), would be greatly increased in quantity and also made to include other salts, including those of potassium, sodium sulphate, magnesium chloride, &c.

Further information on these deposits will be found in the works of Sturzer (Nitrate of Soda, 1887; edited by Wagner) and Billingham (Estudio sobre la Geografia de Tarapaca, and Chem. Zeit. 11, 752), and in the various Consular reports to the British and United States Governments.

The production of sodium nitrate from July 1, 1921, to June 30, 1922, was 1,071,297 tons, against 2,772,254 tons in 1913. Exports for that year amounted to only 502,481 tons, of which about 50 p.c. went to the United States (J. Soc. Chem. Ind. 1923, 42, 1170).

Bearing on the Chile nitrate future is the finding of extensive deposits of potassium nitrate in Cape Colony (J. Soc. Chem. Ind. 38, 361, T.).

The manufacture from synthetic calcium nitrate by precipitation with sodium sulphate is easy if the salts are mixed at 150°–175°, *i.e.* 175°, so as to throw out the anhydrous CaSO₄; 93 p.c. yield is obtained (J. Soc. Chem. Ind. 1915, 1141).

Sodium nitrate is obtained when sodium carbonate or hydroxide is dissolved in nitric acid, or when common salt is boiled with that acid. On the large scale, however, it is always obtained from the natural product by repeated crystallisation. The last traces of chloride are best removed by adding a small quantity of nitric acid to the boiling saturated solution of the salt, and recrystallising.

Properties.—The pure salt forms transparent,

colourless, anhydrous rhombohedra, whose angles closely approximate to right angles, whence its name 'cubic nitre.' For the crystal structure of sodium nitrate, *see* W. G. Wyckoff (Physical Rev. 1920, 16, 149; Chem. Soc. Abstr. 1920, ii. 756). Its sp.gr. is 2.26. It fuses at 316° (Carnelley), 315.1° (Menzies and Dutt), 390° (Briscoe and Magdin) (J. Chem. Soc. 123, 1608), and the sp.gr. of the fused salt is 2.12–0.0007t between 320° and 515°; at higher temperatures—lower than that at which potassium nitrate decomposes—it evolves oxygen with production of the nitrite (*see* below), and on further heating it gives off nitrogen and nitrous fumes, leaving a residue of sodium monoxide and peroxide. The salt as usually obtained is hygroscopic; but, according to Gentile (Dingl. poly. J. 118, 203), this is due to the presence of the nitrates and chlorides of calcium and magnesium, and is not observable in the pure salt. Mixtures of sodium and potassium nitrates have a minimum m.p. of 225.7°, when the p.c. sodium nitrate is 45 (Briscoe and Magdin, *l.c.*).

According to Ditte (Compt. rend. 80, 1164) 100 parts of water dissolve the following proportions of the salt:—

At 0°	66.69	At 18°	83.62
2°	70.97	21°	85.73
4°	71.04	26°	90.33
8°	75.65	29°	92.93
10°	76.31	36°	99.39
13°	79.00	51°	113.63
15°	80.60	68°	125.07

The sp.gr. and thermal expansions and vapour pressures of the solutions are found in Landolt Bornstein (Phys. Chem. Tabellen, 4th ed. 256, 289 and 412). When saturated at 0° the solution may be cooled to –15.7° without crystallisation; but at that temperature the salt separates out in laminated plates built up of fine needles lying side by side. A hydrate of the composition $\text{NaNO}_3 \cdot 7\text{H}_2\text{O}$ appears to exist (Ditte, *l.c.*). For the heat of dilution and specific heat of sodium nitrate, *see* Richards and Rowe (J. Amer. Chem. Soc. 1921, 43, 770; Chem. Soc. Abstr. 1921, ii. 380).

Sodium nitrate dissolves in glycerol, but is almost insoluble in absolute alcohol; 100 parts of alcohol of 16.4 p.c. dissolve 21.25 parts of the salt (Pohl, Sitz. Ber. 6, 600).

Applications.—It is used for many of the purposes for which the potassium salt is employed; but its hygroscopic nature renders it inapplicable to the manufacture of gunpowder or fireworks, &c. For the use of sodium nitrate in the manufacture of ammonium sulphate, *see* Dawson (Chem. Soc. Trans. 1918, 675, A. ii. 363). For the making of nitric acid, for supplying that acid in the sulphuric acid manufacture, and as a manure, it has, however, entirely replaced potassium nitrate. It is also the principal source of that salt, which is obtained from it by double decomposition with the potassium chloride of Stassfurt.

For manurial purposes it is important that it should be free from perchlorates, chlorates, and iodates, as they are toxic to plant life (*see* J. Soc. Chem. Ind. 1897, 152; 1898, 168; 1899, 1141; 1900, 361. *See also* Tacke and Brüne, Chem. Soc. Abstr. 1913, i. 1432; Potter and Snyder, *ibid.* 1916, i. 459; Gorski, *ibid.* 1919, i.

616; Howard, *ibid.* 1920, i. 416). The perchlorate varies from traces up to 1.65 p.c., and occasionally still more. Methods of determining the chlorine salts are given in J. Soc. Chem. Ind. 1897, 163; 1898, 275, 694, 795; 1900, 361, and for determining the iodate in J. Soc. Chem. Ind. 1900, 277. For the estimation of sodium nitrate, *see* Allen (Eighth Inter. Cong. App. Chem. 1912, 1, 19; Chem. Soc. Abstr. 1913, ii. 726). For the estimation of nitrogen in sodium nitrate, *see* Butt (J. Ind. Eng. Chem. 1920, 12, 352; Chem. Soc. Abstr. 1920, ii. 386). The estimation of perchlorates in sodium nitrate, *see* Monnier (Chem. Soc. Abstr. 1916, ii. 639).

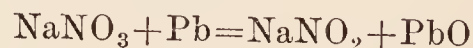
Sodium nitre NaNO_3 , synonymous with sodium nitrate (*see* p. 238). This term distinguishes the old nitre which is KNO_3 from the more recent Chile saltpetre NaNO_3 .

Sodium nitrites, NaNO_2 and Na_2NO_2 .

1. *Sodium nitrite* NaNO_2 occurs native in small amounts in Chile saltpetre, and is frequently found, although only in traces, in mineral waters and in soil extracts where it is produced from decaying organic matter by certain bacteria.

It is prepared artificially by heating sodium nitrate, either alone or mixed with deoxidising substances, metallic lead, iron filings, or graphite being those usually employed; other reducing agents as sulphur (Eng. Pat. 4743 of 1896, Paul and Read Holliday), calcium sulphide (tank waste), barium sulphide, zinc blende, and galena have also been employed. The salt prepared in this way, however, invariably contains some undecomposed nitrate, and also some Na_2O by evolution of nitrous fumes and nitrogen, and is therefore purified where necessary by crystallisation. The pure salt is best made by decomposing a solution of silver nitrite with an equivalent amount of sodium chloride, or by passing the nitrous fumes evolved from a mixture of nitric acid and starch into a solution of caustic soda or sodium carbonate (Divers, Chem. Soc. Trans. 1899, 86). It may also be obtained by the electrolytic reduction of the nitrate, but the yield obtained is only 60 p.c. of the theoretical (Muller, Zeitsch. Elektro. Chem. 1903, 9, 955). It is also now produced from atmospheric nitrogen and oxygen, and is prepared 96–99 p.c. pure (Chem. & Met. Eng. January 15, 1919, Advert. p. 73, Marden, Orth and Hastings). For the electrolysis of solutions of sodium nitrite, *see* Jeffery (Trans. Faraday Soc. 1921, 16, 453; Chem. Soc. Abstr. 1921, ii. 374; *see also* Chem. Soc. Abstr. 1922, 611).

Technical manufacture.—On the large scale, sodium nitrite is made by the first-named method. The lead employed must be as free as possible from zinc and antimony, and is rolled out into thin sheets previous to use. The theoretical amount of lead required for the decomposition of 100 parts of sodium nitrate according to the equation—



is 243 parts, but in practice an excess is invariably used.

The sodium nitrate (100 kilos.) is melted in a cast-iron vessel fitted with a mechanical stirrer. As soon as the whole is in a state of quiet fusion, 250 kilos. of lead are added, which rapidly oxidises to yellow PbO . After a short time

more lead is added, and the mixture kept well stirred for three-quarters of an hour, the whole operation lasting about $3\frac{1}{2}$ hours. Thorough stirring is essential, as if any of the mixture is allowed to cake on the sides of the vessel, the latter is soon corroded and rendered useless.

The product is extracted with water in wrought-iron vessels, provided with stirrers, until the solution has a density of 36° – 39° Baumé. The alkaline liquid is then carefully neutralised with dilute nitric acid, and allowed to settle. The clear solution is evaporated to 42° – 43° Baumé, allowed to stand three or four hours to clarify, and then run into lead-lined wooden tanks where crystallisation takes place. The crystals obtained contain, after being dried at 60° , 97–98 p.c. of sodium nitrite.

The mother-liquors can be evaporated several successive times after addition each time of a little fresh liquid from the vats. The purity of the nitrite thus obtained continually diminishes, as the following figures show:—

	Percentage of NaNO ₂ contained in the crystals after drying at 60°
Crystals from 1st evaporation	97 to 97.5 p.c.
„ 2nd „	96.8 to 97 „
„ 3rd „	96.2 to 96.5 „
„ 4th „	96 to 96.2 „

If a higher content of nitrite be required, the salt must be recrystallised. When the crystals obtained from the liquid show less than 96 p.c. of NaNO₂, the mother-liquor is evaporated separately in a second pan, and produces crystals containing 86–94 p.c. of nitrite, which are employed to strengthen the fresh lye. The solution separated from these is further concentrated in a third pan, and yields crystals containing 50–75 p.c. of nitrite. Those containing above 65 p.c. NaNO₂ are returned to the second pan, and the remainder are fused up again with lead in the manner described above. An analysis of the final mother-liquor drainings gave:

	p.c.
Caustic soda	10.89
Sodium carbonate	22.00
Sodium nitrite	20.52
Sodium nitrate	16.23
Sodium chloride	6.05
Sodium sulphate	17.39
Insoluble	7.23
	100.31

For details of the manufacture, *see*, further, Turner (J. Soc. Chem. Ind. 1915, 34, 585).

Properties.—Sodium nitrite forms small rhombic crystals, which usually possess a faint yellow colour, although according to Boguski (J. Russ. Phys. Chem. Soc. 1899, 31, 543) the pure dry salt is colourless. The sp.gr. is 2.157. The crystals melt at 271° (Divers) and dissolve easily in water (1 part of the salt dissolves in 1.2 parts of water at 15°) forming a yellowish solution which is alkaline to litmus. The salt is very sparingly soluble in absolute alcohol, 100 parts of this solvent dissolving only 0.31 part of sodium nitrite at 19.5° . The solubility of sodium nitrite and its mixtures from sodium nitrate, *see* Oswald (Eighth Inter. Cong. App.

Chem. 1912, 2, 205; J. Chem. Soc. Abstr. 1913, ii. 701). For the standardisation of sodium nitrite with *p*-nitroaniline, *see* Bell (Chem. Met. and Eng. 1920, 22, 1173; from Chem. Zentr. 1921, ii. 94; Chem. Soc. Abstr. 1921, ii. 216).

For the density of sodium nitrite solutions, *see* Boguski, Anz. Krak. Akad. 1898, 123. For conductivity measurements, *see* Roczowski and Niementowsky, Zeitsch. physikal. Chem. 1897, 22, 147, and Schumann, Ber. 1900, 33, 532.

The action of copper on sodium nitrite, *see* Peters (Zeitsch. anorg. Chem. 1919, 107, 313; Chem. Soc. Abstr. 1919, ii. 413). For the velocity of reaction of sodium nitrite on blood, *see* Marshall (Proc. Roy. Soc. Edin. 1918, 39, 149; Chem. Soc. Abstr. 1919, i. 605).

Uses.—Sodium nitrite is largely used in the manufacture of coal-tar colours, especially the diazo colours, and also in the calico-printing industry in the preparation of certain colours, such as paranitraniline red, which are developed on the fibre.

2. *Disodium nitrite* Na₂NO₂, an additive compound of sodium nitrite and sodium, may be prepared by dissolving a known weight of sodium in anhydrous liquid ammonia and adding freshly fused, finely divided sodium nitrite in the proportion of one mol. to each atom of sodium. The completion of the reaction is marked by the discharge of the deep blue colour. Disodium nitrite settles out as a yellow precipitate. By the electrolysis of sodium nitrite, using platinum electrodes, a yellow deposit of disodium nitrite is obtained on the cathode. The compound is very readily decomposed by water (E. V. Maxted, Chem. Soc. Trans. 1917, 111, 1016–1019).

Sodium nitroprusside Na₂[Fe(NO)(CN)₅].2H₂O was discovered by Playfair in 1850. In order to prepare it, powdered potassium ferrocyanide is treated with twice its weight of concentrated nitric acid, previously diluted with its own volume of water. The mixture turns brown, and carbon dioxide, cyanogen, nitrogen, and hydrocyanic acid are evolved. As soon as solution is complete the liquid is warmed on a water-bath until a few drops give a slate-coloured precipitate on the addition of ferrous sulphate. It is then allowed to cool, when crystals of potassium nitrate separate out. The solution separated from the crystals is neutralised with sodium carbonate, filtered, and evaporated, when ruby-red crystals of sodium nitroprusside are obtained, which must be recrystallised to free them from admixed nitrate.

Another method of preparation consists in mixing a concentrated aqueous solution of ferrous sulphate with a solution containing equal parts of potassium cyanide and sodium nitrite, and allowing the mixture to remain at the ordinary temperature for five hours. Ferric hydroxide is deposited, and nitrogen and nitric oxide evolved. The liquid is then heated to 25° for a short time, made slightly alkaline with caustic soda, filtered, and the sodium nitroprusside obtained by evaporation and crystallisation.

Sodium nitroprusside forms ruby-red rhombic crystals, which contain two molecules of water of crystallisation. It dissolves in $2\frac{1}{2}$ parts of water at 15° , and in a smaller quantity of hot water. The solution decomposes on exposure to light with separation of Prussian blue and evolution of nitric oxide.

A concentrated solution is used as a reagent for the detection of small amounts of sulphur existing in the form of alkaline sulphide, a deep violet colour being produced. The colour is sufficiently intense to be noticeable in a solution containing only 0.0000018 gm. of H_2S in the form of ammonium sulphide, and by employing a capillary tube when applying the test one-tenth of this amount can be detected. The solution to be tested must be as concentrated as possible, and an excess of caustic soda in the liquid should be avoided, as this tends to prevent the development of the colour. The most suitable alkali to employ is ammonia, an excess of which has no such retarding action (Reichard, *Zeitsch. anal. Chem.* 1904, 43, 222). The nature of the coloured compound produced is at present a matter of uncertainty, but it is probably represented by the formula $\text{Na}_3[\text{Fe}(\text{NO} \cdot \text{SNa})(\text{CN})_5]$ as the action of thiourea on sodium nitroprusside yields a compound $\text{Na}_3[\text{Fe}(\text{NO} \cdot \text{NH} \cdot \text{CS} \cdot \text{NH}_2)(\text{CN})_5]$ which is a carmine red powder, closely resembling the substance formed from nitroprussides and sulphides.

Sodium nitrosotrisulphonate, *see* Traube (*Ber.* 1913, 46, 2513; *Chem. Soc. Abstr.* 1913, ii. 947).

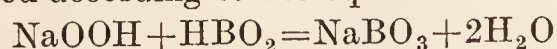
Sodium oxides. The oxidation of sodium was studied by Davy (*Phil. Trans.* 1808), Gay-Lussac and Thenard (*Recherches Physico-chem.* 1, 132), Harcourt (*J. Chem. Soc.* 1861, 14, 267), Holt and Sims (*J. Chem. Soc.* 1894, 65, 440), de Focrand (*Compt. rend.* 1898, 364, 514). The formation of suboxides as Na_4O and Na_3O is not definite; all are agreed upon the formation of the monoxide Na_2O (*see* p. 237), the base of all the common sodium salts, and the real soda of the chemists prior to Davy; the end product of oxidation appears to be sodium peroxide Na_2O_2 (*see* below), but still higher oxides Na_2O_3 have been described by Johannis (*Compt. rend.* 1893, 116, 1370; *Ann. Chim.* 1906, [8] 7, 5), and even Na_2O_4 . For the heats of combination of sodium oxide with acidic oxides, *see* Mixter (*Amer. J. Sci.* 1913, [iv.] 36, 55; *Chem. Soc. Abstr.* 1913, ii. 756).

Sodium perborate. *See* vol. i. 649; and for use in sterilising, *see* Vol. II. 538. According to Foerster (*Zeitsch. angew. Chem.* 1921, 34, 354) the salt, which was generally represented as $\text{NaBO}_3 \cdot 4\text{H}_2\text{O}$, has the composition



On drying at 120° in a vacuum it consists mainly of $(\text{NaBO}_2)_2\text{O}_2$, which loses oxygen on treatment with water (and has properties which differ from those of NaBO_3), and all methods of preparation of this form of sodium perborate are based upon the reaction $\text{NaBO}_2 + \text{H}_2\text{O}_2 = \text{Na}[\text{BO}_2 \cdot \text{H}_2\text{O}_2]$.

The other form of sodium perborate may be prepared according to the equation



Le Blanc and Zellmann (*Zeitsch. Elektrochem.* 1923, 29, 192).

Sodium percarbonate. *See* Vol. V. 94.

Sodium perchlorate NaClO_4 . *See* Vol. II. 214; occurrence in Chile saltpetre, *see* this vol. under *Sodium nitrate* (pp. 238 and 239).

Sodium permanganate NaMnO_4 . *See* under *Manganese*; for use in sterilising, *see* Vol. II. 544. It has largely supplanted the potassium salt (*J. Soc. Chem. Ind.* 1920, R. 7). For the electrolytic preparation of sodium permanganate,

see Henke and Brown (*J. Phys. Chem.* 1920, 24, 608; *Chem. Soc. Abstr.* 1921, ii. 115). The preparation of sodium permanganate from ferromanganese, *see* Wilson, Horsch and Youtz (*J. Ind. Eng. Chem.* 1921, 13, 763; *Chem. Soc. Abstr.* 1921, ii. 643).

Sodium peroxides, Na_2O_2 , and others.

Sodium peroxide or dioxide Na_2O_2 is obtained when the metal is completely burned in air or oxygen. It is now made on the large scale according to Castner's process (*Eng. Pat.* 20003, 1891), which consists in placing sodium on aluminium trays loaded on to small waggons, which are then run through an iron tube, provided at each end with tightly-closing iron doors, set in a furnace and heated to 300° . A current of dry air, free from carbon dioxide, is passed through the tube, the peroxide produced being withdrawn at one end and fresh charges of sodium introduced at the other. The technical product thus obtained contains about 93 p.c. of sodium peroxide. For an apparatus for sodium peroxide fusions, *see* Hodsman (*J. Soc. Chem. Ind.* 1921, 46, 74 T.; *Chem. Soc. Abstr.* 1921, ii. 345).

Pure sodium peroxide is pale yellow; its sp.gr. is 2.27. It absorbs moisture rapidly from the air to form a snow-white hydrate $\text{Na}_2\text{O}_2 \cdot 8\text{H}_2\text{O}$ (Jaubert, *Compt. rend.* 1901, 132, 35). It absorbs carbon dioxide and water vapour from expired air with formation of sodium carbonate and liberation of oxygen, and a mixture of this oxide with potassium peroxide is used in life-saving apparatus to regenerate air contaminated by respiration. The rapidity with which the hydrating peroxide liberates oxygen may be augmented by certain catalysts—ferric hydroxide having a slight action but copper oxide having an enormous effect. With CO it yields sodium carbonate, and with N_2O and NO sodium nitrite. Charcoal and the alkaline earth carbides reduce it partially to metallic sodium at a temperature of 300° – 400° (Bamberger, *see* p. 233, col. 1, par. 4). Although sodium peroxide is not decomposed when heated alone, it readily gives up oxygen to other substances mixed with it, and hence is largely used in the analysis of many refractory minerals, such as pyrites and chromite; as fused sodium peroxide acts most energetically on platinum, iron, &c., it is necessary to use crucibles of nickel, as this is less attacked than other metals. Special precautions must be taken in handling; it must never be placed on paper or wood, nor be allowed to fall on to straw or sawdust, as the heat of hydration arising from the moisture natural to these substances is sufficient to cause a spontaneous and most violent ignition. If glass or porcelain articles cannot be used for its manipulation, there is nothing better than clean dry iron or nickel. Tinned iron, lead coated iron, and galvanised iron are not so good, as none of those metals withstands the action of the peroxide and moisture. Under no conditions may copper or brass instruments be used, since the copper is readily oxidised to red Cu_2O , which acts as a most energetic catalyst that would immediately destroy all peroxide compounds if the peroxide were to be dissolved in any aqueous solution. For the action of carbon oxides on sodium peroxide, *see*

Zenghelis and Horsch (Compt. rend. 1916, 163, 388; Chem. Soc. Abstr. 1916, ii. 616). The action of hydrogen sulphide with sodium peroxide, *see* Zenghelis and Horsch (Compt. rend. 1916, 163, 440; Chem. Soc. Abstr. 1916, ii. 612). For the ignition of a mixture of aluminium and sodium peroxide by means of water, *see* Ohmann (Ber. 1920, 53, [B], 1427; Chem. Soc. Abstr. 1920, ii. 691).

Sodium peroxide dissolves readily in water with liberation of so much heat that particles may change from yellow to orange; yet if a particle becomes coated with a film of the hydrate $\text{Na}_2\text{O}_2 \cdot 8\text{H}_2\text{O}$ then it will dissolve only slowly and the heat evolved is steadily dissipated. By sprinkling the peroxide powder upon the surface of water kept stirred the solution may be effected without decomposition.

Sodium peroxide is employed in the laboratory as an oxidising agent in mineral analyses, and in calorimetric determinations, and for the manufacture of oxygen for clinical purposes. For the use of sodium peroxide in thermochemistry, *see* Mixer (Amer. J. Sci. 1917, [iv.] 43, 27; Chem. Soc. Abstr. 1917, ii. 123). It is used for the manufacture of other peroxides, as calcium peroxide and zinc peroxide, for medicinal purposes. Its principal use is for preparing dilute solutions of hydrogen peroxide for bleaching wool, silk, straw, and sometimes fine cotton articles. For methods of analysis, *see* Fischer's Jahresb. 1905, 432; J. Soc. Chem. Ind. 1919, A. 10 and 575.

Analysis of sodium peroxide.—Two methods are available for the estimation of the active oxygen in sodium peroxide, viz. gasometric and volumetric. For the former 0.2 to 0.6 grm. of the powder, weighed in a closed tube, is introduced in a small flask fitted with a fine dropping funnel and connected with a Bunte burette; 15 c.c. of 1:10 sulphuric acid and 3 drops of a saturated solution of cobalt nitrate are slowly added from the dropping funnel, and afterwards the flask is gently warmed. The gas evolved may be measured over brine or potassium hydroxide solution, the latter having the advantage of absorbing any carbon dioxide. The difficulty with the permanganate titration method is the decomposition brought about by the heat of hydration of the sodium peroxide; this may be overcome by the following method, which gives results identical with those of the gasometric method: From 0.2 to 0.4 grm. of the peroxide is mixed in a mortar with 3 to 5 grms. of powdered boric acid. Then 100 c.c. of water and 10 c.c. of 1.5 sulphuric acid are added, and the resultant hydrogen peroxide is titrated in the usual manner with 0.1N potassium permanganate solution (E. Bosshard and E. Furrer, Helv. Chim. Acta, 1924, 7, 486; Analyst, 1924, 49, 353; *see also* Milbauer, Chem. Soc. Abstr. 1919, ii. 31; 1922, ii. 520).

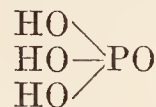
By exposing the peroxide to moist air free from carbon dioxide, or by the cautious evaporation of its solution in cold water, tabular hexagonal crystals of a hydrate $\text{Na}_2\text{O}_2 \cdot 8\text{H}_2\text{O}$ can be obtained, which on standing over sulphuric acid lose water, forming the dihydrate $\text{Na}_2\text{O}_2 \cdot 2\text{H}_2\text{O}$. The octahydrate is also produced by adding $1\frac{1}{2}$ –2 times its volume of alcohol to a solution of caustic soda and hydrogen peroxide (Schöne, Annalen, 1878, 193,

241). The hydrate dissolves in cold water without decomposition, but on heating the solution oxygen begins to be evolved at 30° – 40° , the decomposition of the salt being complete at 100° .

Other peroxides have been described, especially sodium sesquioxide Na_2O_3 (Johannis, Ann. Chem. 1906, viii. 7, 75), and the tetroxide Na_2O_4 , also sodylhydroxide NaO_2H (J. Tafel, Ber. 1894, 27, 816 and 2297), but none of these is prepared commercially.

Sodium phenate NaOC_6H_5 . *See* Vol. II. 57.

Sodium phosphates (Ortho). These salts are all derived from orthophosphoric acid—



Our knowledge of the various sodium phosphates is largely due to Graham (Phil. Trans. 1833, 253). The qualitative tests distinguishing the orthophosphates from the pyro- and metaphosphates are (1) silver nitrate gives with orthophosphates a yellow precipitate, viz. Ag_3PO_4 ; (2) the orthophosphates do not precipitate an aqueous solution of albumen. For the emission of electrons by sodium phosphate, *see* Horton (Proc. Camb. Phil. Soc. 1914, 17, 414; Chem. Soc. Abstr. 1914, ii. 412). For the constitution of the alkali phosphates and some double phosphates, *see* Smith (J. Soc. Chem. Ind. 1917, 36, 420; Chem. Soc. Abstr. 1917, ii. 309).

Trisodium phosphate Na_3PO_4 is obtained by adding excess of caustic soda to a warm strong solution of hydrogen sodium phosphate, and crystallising by cooling. It may also be prepared by fusing hydrogen disodium phosphate with excess of soda and dissolving and crystallising. It forms non-efflorescent six-sided prisms of the composition $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$.

According to Mohr (Amer. J. Sci. [iii.] 14, 281), their sp.gr. is 1.620. They fuse at about 73.4° ; at 100° they lose 11 molecules, but they retain the last until the heat approaches redness. The residual anhydrous salt has a sp.gr. 2.536. The crystals dissolve in about 10 times their weight of water at 15° . The solution reacts strongly alkaline. In solutions weaker than decinormal almost the whole of the salt is hydrolysed (Salm, Zeitsch. physikal. Chem. 1907, 57, 471; Shield, *ibid.* 1893, 12, 167). In consequence of this hydrolysis a solution of the salt is decomposed by all acids, even by CO_2 , with formation of disodium phosphate and the salt of the acid in question. Tribasic sodium phosphate is used in place of sodium carbonate in some photographic developers, and it has been proposed to use the melting-point of the dodecahydrated salt (73.4°) as a standard for use in calibrating thermometers.

A heptahydrate has been prepared by Hall (J. Chem. Soc. 1887, 97).

Disodium hydrogen phosphate Na_2HPO_4 occurs in urine, in which it was discovered by Haupt in 1740, and was at one time prepared from it under the name *sal mirabile perlatum*.

It may be prepared by adding sodium carbonate to crude phosphoric acid until alkaline, and filtering, concentrating, and crystallising the solution. It is usually prepared from the acid calcium phosphate made by the action of sulphuric acid on bone ash; for this purpose the hot

solution is treated with sodium carbonate until effervescence ceases, and the solution of hydrogen sodium phosphate thus produced is filtered from the precipitated tricalcium phosphate, and is concentrated and crystallised. For the electrolytic reduction of sodium hydrogen phosphate, see Wenger and Heinen (Ann. Chim. anal. 1914, 19, 209; Chem. Soc. Abstr. 1914, ii. 777).

The salt crystallises in large, colourless, transparent monoclinic prisms of the composition $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$, and sp.gr. 1.5235 at 15° (Stolba, J. Pharm. Chim. 97, 503). On exposure to the air they soon effloresce, and become opaque by formation of the heptahydrate. Sharp breaks are observed in the heating and cooling curves for the dodecahydrate at 29.6°, due to a change of phase in that substance, that is, two forms of $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ exist, of which one is stable from 0° to 29.6°, and the other is stable only from 29.6° upwards. But when the temperature reaches 35.0 the crystals melt. The salt kept at 35° and exposed to the air loses moisture and deposits monoclinic crystals of $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$. This heptahydrate cannot exist above the temperature 48.09°. Between 48.09° and 94.97° only the dihydrate $\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$ can exist. Above 94.97° only the anhydrous salt is known. When dried over sulphuric acid, or heated for some time to 45°, they become anhydrous.

On further heating sodium pyrophosphate is formed, the transformation being complete at 300°:



The salt dissolves readily in water, and supersaturated solutions are formed easily. The solubilities of the various hydrates have been determined by a number of observers, and a summary from Phys. Chem. Tabellen Landolt Börnstein Roth (1912), p. 486, gives the saturations at the following temperatures when the liquid is in equilibrium with the various hydrates named:—

Temp. °C	Solid	100-grm. solution contains grms. of Na_2HPO_4
0.0	$\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$	2.44
10.0	"	3.75
17.0	"	4.21
20.0	"	8.51
25.0	"	11.13
30.0	"	19.20
35.4	$\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$	31.55
40.0	"	35.4
52.7	$\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$	45.8
59.0	"	47.6
70.0	Na_2HPO_4	48.7
78.5	"	48.9
85.0	"	49.3
99.0	"	49.7
105.0	"	45.2

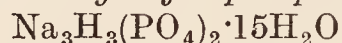
The saturated solution boils at 105°. The aqueous solutions react alkaline to litmus. The salt is insoluble in alcohol. For the solubility of sodium hydrogen phosphate and of its hydrates, see Menzies and Humphery (Eighth Inter. Cong. App. Chem. 1912, 2, 175; Chem. Soc. Abstr. 1913, ii. 701). Disodium hydrogen phosphate dodecahydrate, see Hammick, Goadby and Booth (Chem. Soc. Trans. 1920, 1589). The dehydration of sodium hydrogen phosphate,

see Balareff (Zeitsch. anorg. Chem. 1916, 97, 147; Chem. Soc. Abstr. 1917, ii. 88).

Hydrogen disodium phosphate is used in certain photographic toning solutions, and to some extent in calico-printing and for weighting silk, and in medicine as a mild purgative.

Sodium dihydrogen phosphate NaH_2PO_4 is prepared by adding phosphoric acid to a solution of the disodium salt until the liquid ceases to give a precipitate with barium chloride. On cooling the hot strong solution it is obtained in rhombic crystals of sp.gr. 1.90, containing 2 molecules of water, which are very soluble in water but insoluble in alcohol. A hydrate $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ has also been prepared, sp.gr. 2.040. On heating to 100° the salt becomes anhydrous, at 210° it is converted into the acid pyrophosphate $\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$, and on further heating yields a mixture of metaphosphate and trimetaphosphate (Knorre, Zeitsch. anorg. Chem. 1900, 24, 369). According to Herxheimer (Klin. Woch. 1922, i. 480, from Chem. Zentr. 1922, i. 985), phosphoric acid given as sodium dihydrogen phosphate has a favourable effect on the growth of the human body and energy production (Chem. Soc. Abstr. 1922, i. 970).

Trisodium trihydrogen phosphate



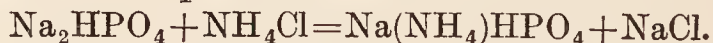
has been obtained by Filhol and Senderens (Compt. rend. 93, 388) by making a solution of caustic soda and phosphoric acid neutral to litmus, and then concentrating and crystallising. Joulie obtained the same salt but anhydrous by crystallising at 45°–50°, and recommended it for medicinal purposes (J. Chem. Soc. Abst. 1902, ii. 318).

Sodium ammonium hydrogen phosphate



This salt occurs in urine. It was well known to the alchemists under the names of 'microcosmic salt,' 'fusible salt of urine,' and 'essential salt of urine,' and was employed by them as a source of phosphorus. It still goes by the first name. It has also been met with in nature as the mineral *stercorite*, found in some guano deposits.

The salt is obtained artificially by mixing hot solutions of 5 parts disodium phosphate and 2 parts ammonium phosphate, and allowing the solution to cool. Another method consists in mixing hot solutions of 7 parts disodium phosphate and 1 part of ammonium chloride:



The crystals obtained by this latter process contain a little sodium chloride, and must be purified by recrystallisation from hot water containing ammonia.

Microcosmic salt forms transparent, monoclinic crystals of sp.gr. 1.55, which possess a saline taste. It loses ammonia on exposure to air. The aqueous solution of the salt has an alkaline reaction and loses ammonia on boiling. On heating, the crystals melt easily and evolve water and ammonia, being converted into sodium dihydrogen phosphate. On further heating, more water is evolved and a residue of sodium hexametaphosphate remains as a clear, glassy mass. Microcosmic salt when fused on a fine platinum wire possesses the property of dissolving all metallic oxides and salts, but silica free or originally combined does not dissolve; originally combined silica

appears as a gelatinous mass, the characteristic so-called 'silica skeleton.'

Sodium metaphosphates. A large number of these salts have been prepared. The different classes are known as mono-, di-, tri-, and hexa-metaphosphates, and are to be regarded as derived from the simple metaphosphoric acid HPO_3 and its polymers $(\text{HPO}_3)_n$.

According to Tamman (Zeitsch. physikal. Chem. 1890, 6, 122; J. pr. Chem. 1892, [ii.] 45, 417) certain of the hexametaphosphates exist in metameric forms. The different classes of the sodium metaphosphates are represented in the following table:—

$\text{Na}_2(\text{PO}_3)_2$	sodium dimetaphosphate
$\text{Na}_3(\text{PO}_3)_3$	„ trimetaphosphate
$\text{Na}_6(\text{PO}_3)_6$	„ hexametaphosphate
$\text{Na}_2[\text{Na}_4(\text{PO}_3)_6]$	metameric sodium hexa- meta-phosphates
$\text{Na}_4[\text{Na}_2(\text{PO}_3)_6]$	
$\text{Na}_5[\text{Na}(\text{PO}_3)_6]$	
NaPO_3	Three insoluble monometa- phosphates.

According to Warschauer (Zeitsch. anorg. Chem. 36, 137) the so-called dimetaphosphate is in reality a tetrametaphosphate. All the metaphosphates of sodium are soluble in water except the monometaphosphates. The tri- and tetra- salts may be distinguished from one another by the action of barium chloride or lead nitrate, the latter class giving white precipitates with these reagents. The hexametaphosphates are glassy amorphous salts, which yield precipitates with solutions of salts of the alkaline earths and heavy metals. For further details concerning the sodium metaphosphates, reference must be made to the original papers. See Tamman (*l.c.*), Knorre (Zeitsch. anorg. Chem. 1900, 24, 378), and Warschauer (*l.c.*), where an account of the literature on the subject is given. See also P. Pascal, Compt. rend. 1923, 176, 1398.

Sodium polyphosphate $\text{Na}_4\text{P}_6\text{O}_{17}$. Described by Smith (J. Soc. Chem. Ind. 1917, 419) by evaporating a mixed solution of caustic soda and phosphoric acid, is a fused glassy mass that is so exceedingly corrosive to glass, porcelain, nickel, platinum and silica that it might be of service in attacking minerals otherwise difficult to dissolve.

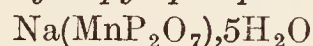
Sodium pyrophosphates.

Normal sodium pyrophosphate $\text{Na}_4\text{P}_2\text{O}_7$ is produced, as stated (p. 244, col. 1, par. 3), by heating the disodium hydrogen orthophosphate to 300° , when it remains as a white, glassy mass of sp.gr. 2.37 (Clarke), which melts at about 880° (at 970° Landolt, Bornstein, 4th ed. 222). The salt dissolves in water, yielding a solution having an alkaline reaction, and can be obtained by evaporation in monoclinic crystals of sp.gr. 1.82 containing 10 mols. of water. The aqueous solution is not converted into the orthophosphate by boiling alone, but the presence of an acid, even such a weak one as acetic acid, is sufficient to effect the change on heating. For the double pyrophosphate of iron and sodium, see Oliveri-Mandala (Gazz. chim. ital. 1921, 51. i. 130; Chem. Soc. Abstr. 1921, ii. 338).

Sodium pyrophosphate is occasionally used in medicine in place of the disodium orthophosphate, and also serves as the material for the preparation of the insoluble metallic

pyrophosphates and their double salts. It has also been recommended as a preservative for solutions of hydrogen peroxide. The purity of sodium pyrophosphate, see Kolthoff (Pharm. Weekblad, 1920, 57, 474; Chem. Soc. Abstr. 1920, ii. 620). The action of hydrogen peroxide with sodium pyrophosphate, see Society of Chemical Industry in Basle (Chem. Soc. Abstr. 1916, ii. 616). For the toxicity of sodium pyrophosphates, see Symes and Gardner (Bio-Chem. J. 1915, 9, 9; Chem. Soc. Abstr. 1915, ii. 482). According to Rosenheim and Triantaphyllides (Ber. 1915, 48, 582), it has long been known that the insoluble pyrophosphates of many metals dissolve in alkaline pyrophosphates to give solutions which fail to show many of the reactions of the metals. Some of the salts of the complex metallopyrophosphoric acids are described. They are comparable with Weinland and Ensgraber's salts of the ferriphosphoric acid (Chem. Soc. Abstr. 1914, ii. 132).

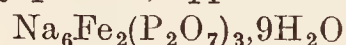
Sodium manganipyrophosphate



(Christensen, Chem. Soc. Abstr. 1884, 399) is obtained by dropping a solution of manganese sesquioxide in cold concentrated hydrochloric acid into a saturated solution of sodium pyrophosphate. Potassium forms two salts, $\text{K}(\text{MnP}_2\text{O}_7) \cdot 5\text{H}_2\text{O}$, pale violet, stable below 10° , and the trihydrate, which is pale red, and only decomposed by boiling water. The ammonium salt $\text{NH}_4(\text{MnP}_2\text{O}_7) \cdot 3\text{H}_2\text{O}$ is pale violet, and is hydrolysed by cold water. From it may be obtained the pink silver salt $\text{Ag}(\text{MnP}_2\text{O}_7) \cdot 3\text{H}_2\text{O}$, and the pink barium salt $\text{Ba}(\text{MnP}_2\text{O}_7)_2 \cdot 5\text{H}_2\text{O}$. They are almost insoluble in cold water.

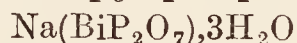
Salts of chromipyrophosphoric acid were prepared in a similar manner. Sodium forms a grey octahydrate $\text{Na}(\text{CrP}_2\text{O}_7) \cdot 8\text{H}_2\text{O}$, which passes into a pale green pentahydrate in a few days. Potassium gives the pale green salt $\text{K}(\text{CrP}_2\text{O}_7) \cdot 5\text{H}_2\text{O}$, and ammonium the hexahydrate $\text{NH}_4(\text{CrP}_2\text{O}_7) \cdot 6\text{H}_2\text{O}$, in grey, microscopic columns. In these salts, the complex anion is more sensitive towards hydrolytic agents than in the manganipyrophosphates.

Iron gives two sodium ferripyrophosphates, a reddish-grey powder, approximating to



and a pale grey compound $\text{Na}_3\text{Fe}_4(\text{P}_2\text{O}_7)_5 \cdot 28\text{H}_2\text{O}$ (compare Pascal, Chem. Soc. Abstr. 1908, ii. 193).

Sodium bismuthpyrophosphate



forms microscopic columns. Sodium thallipyrophosphate $\text{Na}_5[\text{Tl}(\text{P}_2\text{O}_7)_2] \cdot 6\text{H}_2\text{O}$

or $\text{Na}(\text{TlP}_2\text{O}_7) \cdot \text{Na}_4\text{P}_2\text{O}_7 \cdot 6\text{H}_2\text{O}$

crystallises in white needles.

Tripotassium molybdenum hexachloride was added to a solution of sodium pyrophosphate at 80° – 90° , when sodium molybdenipyrophosphate $\text{Na}(\text{MoP}_2\text{O}_7) \cdot 12\text{H}_2\text{O}$ separated as a precipitate of brown prisms. Solutions of tervalent uranium and titanium, however, were immediately oxidised, with evolution of hydrogen.

Vanadium ammonium alum gave with alkaline pyrophosphates a flocculent, green precipitate of vanadium pyrophosphate $\text{V}_4(\text{P}_2\text{O}_7)_3 \cdot 30\text{H}_2\text{O}$, which dissolved in excess to give grass-green solutions, from which, however, no complex salts could be crystallised.

Similarly, cobaltic sulphate gave a stable deep green solution in excess of alkaline pyrophosphate, but no crystalline salt. However, the analogous sodium hexammine cobaltipyrophosphate $\text{Na}\{[\text{Co}(\text{NH}_3)_6\text{P}_2\text{O}_7]\}\cdot 11\cdot 5\text{H}_2\text{O}$ is well known (Jørgensen). *Cerium pyrophosphate* $\text{Ce}_4(\text{P}_2\text{O}_7)_3\cdot 12\text{H}_2\text{O}$ also dissolves in excess of sodium pyrophosphate. The authors are able to confirm Carney and Campbell's discovery (Chem. Soc. Abstr. 1914, ii. 583), that cerium and thorium can be quickly and quantitatively separated by reason of the solubility of cerium pyrophosphate in hydrochloric acid (Chem. Soc. Abstr. 1915, ii. 463).

Disodium hydrogen pyrophosphate $\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$ is prepared by heating sodium dihydrogen phosphate NaH_2PO_4 to 200° for several hours, or more easily by dissolving the normal pyrophosphate in glacial acetic acid and precipitating with alcohol. It then forms a white, crystalline powder which dissolves easily in water, giving a solution with an acid reaction. By evaporation it may be obtained crystallised with 4 or 6 mols. of water, this last salt having a sp.gr. 1·848.

A delicate test for alkaline pyrophosphates is furnished by luteocobaltic chloride $[(\text{NH}_3)_6\text{Co}]\text{Cl}_3$, which gives a pale reddish-yellow precipitate with these salts. By means of this reaction $\frac{1}{33\cdot 05}$ part of pyrophosphate can be detected in the presence of ortho- and metaphosphate (Braun, Zeitsch. anal. Chem. 3, 468).

A considerable number of double pyrophosphates of sodium with potassium, calcium, barium, and other metals have been prepared.

Sodium phosphide, see Tomkinson and Barker (Chem. News, 1920, 121, 104, 177; Chem. Soc. Abstr. 1920, ii. 620).

Sodium potassium carbonate $\text{KNaCO}_3\cdot 6\text{H}_2\text{O}$. This crystalline salt, known as Margueritte's salt, is obtained as by-product in the working up of the salts from beet root molasses (Dammar, Anorganische Chemie, 2, 2, 199; see also J. Chem. Soc. 1888, A. 786); it is also obtained by mixing the components and crystallising. The anhydrous salt is used in analytical work for decomposing insoluble sulphates, silicates, etc., because it fuses at a very much lower temperature than either of the components alone.

Sodium potassium tatarate



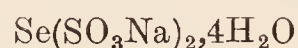
Rochelle salt. See under TARTARIC ACID.

Sodium radium selenate. According to Merch and Eichholz (D. R. P. 256666) it has been shown by Wassermann (Deut. med. Woch, 1911, 2389; Berlin, Klin. Woch, 1912, 4) that compounds of selenium and tellurium exert an electrical action on the cells of living organisms, and it is now found that radium 'adsorption' compounds of selenic, selenious, telluric, or tellurous acids with salts of the alkalis, or alkaline earths, have an eminently specific action on tumour cells. *Radium barium selenate* is precipitated when radium barium chloride (0·4 mg.) in 0·16 c.c. of water is treated with 0·35 c.c. of N-barium chloride solution and 0·35 c.c. of N-sodium selenate; the filtrate is also radioactive. The preparation of *radium barium selenate*, *radium barium tellurate*, *radium barium tellurite*, and of *radium sodium selenate* is also described (Chem. Soc. Abstr. 1913, ii. 374).

Sodium selenite: effect of sodium selenite on protein metabolism, see Cathcart and Orr (J. Physiol. 1914, 48, 113; Chem. Soc. Abstr. 1914, i. 768).

Sodium selenodithionate $\text{Na}_2\text{S}_2\text{SeO}_6$ is produced by adding selenium acetylacetone to a cold concentrated solution of sodium hydrogen sulphite ($2\frac{1}{3}$ mols.), the mixture being shaken until the organic compound is dissolved, and precipitated, by adding alcohol, in colourless, lustrous anhydrous scales, readily soluble in water. Aqueous sulphur dioxide has a similar action on selenium acetylacetone, dissolving it in the cold to a colourless solution containing acetylacetone, extracted by ether, and selenodithionic acid, which slowly decomposes into selenium, sulphur dioxide, and sulphuric acid (Morgan and Drew, Chem. Soc. Trans. 1920, 1462).

Sodium selenodithionate tetrahydrate



is prepared by adding 7 grms. of selenium acetylacetone to 9 grms. of sodium hydrogen sulphite in 30 c.c. of water. The liquid, which becomes appreciably hot, is cooled externally, and after thirty seconds the selenium acetylacetone entirely disappears, becoming replaced by a heavy, colourless, crystalline precipitate of the sodium salt. This product is dissolved in cold water and the filtered solution treated with alcohol, when the purified salt separates in colourless prismatic needles (yield 80 p.c.). This hydrated salt, which is extremely soluble in cold water, very readily forms supersaturated solutions; it effloresced rapidly and passed into the anhydrous salt $\text{Se}(\text{SO}_3\text{Na})_2$ when exposed to a dry atmosphere. Potassium selenodithionate (*l.c.*), the least soluble of the alkali selenodithionates, is obtained by neutralising a 2 N-solution of selenodithionic acid and precipitating with alcohol (Morgan and Smith, Chem. Soc. Trans. 1921, 1067).

Sodium sesquicarbonate, see p. 193.

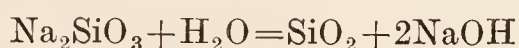
Sodium silicates. The solubility of silica in alkalis was well known to the alchemists, a method for preparing sodium silicate being described as early as 1520. They were also well acquainted with many of the properties of the resulting solution, such as the coagulation which takes place on adding an acid.

These silicates are generally obtained by fusing together sodium carbonate and silica. On cooling, a clear glassy mass remains that when boiled with water slowly dissolves, and if too much water was not added the solution may be a thick syrup, which by evaporation slowly dries to a hard glassy residue. These preparations are quite indefinite, but crystalline hydrated sodium silicates can also be obtained and these are described below. For the preparation and recrystallisation of sodium silicate, see Vesterberg (Chem. Zentr. 1913, i. 777; Chem. Soc. Abstr. 1913, ii. 406).

Sodium metasilicate Na_2SiO_3 , *hydrates*. The theoretical proportions, of freshly precipitated hydrated silica and caustic soda, are heated until dissolved; double the volume of alcohol is added, and a white crystalline powder separates, consisting of one or other of the hydrates with 5, 6, 7, 8, 9 or 10 molecules of water. Some of these hydrates may also be

crystallised from their hot aqueous solution in long needles or plates; the hydrate with $6\text{H}_2\text{O}$ forms monoclinic crystals, that with $9\text{H}_2\text{O}$ rhombic crystals. When rendered anhydrous the residual Na_2SiO_3 melts about 1000° (Kultascheff, *Zeitsch. anorg. Chem.* 1903, 35, 187). The nonahydrate of sodium metasilicate, *see* Vesterberg (*Zeitsch. anorg. Chem.* 1914, 88, 341; *Chem. Soc. Abstr.* 1915, ii. 344). For crystallised sodium silicate, *see* Jordis (*Chem. Zeit.* 1914, 38, 922; *Chem. Soc. Abstr.* 1914, ii. 727). The equilibrium of sodium tungstate with sodium silicate, *see* J. A. N. van Liempt (*Zeitsch. anorg. Chem.* 1922, 122, 175; *Chem. Soc. Abstr.* 1922, ii. 775).

The aqueous solution of the salt has an alkaline reaction owing to hydrolytic dissociation. Kahlenberg and Lincoln (*J. Phys. Chem.* 1898, 2, 81) state that at a dilution of 1 grm. mol. in 48 litres the hydrolysis is complete, according to the equation:



the silica being in colloidal solution. The hydrolysis of the silicates of sodium, *see* Bogue (*J. Amer. Chem. Soc.* 1920, 42, 2575; *Chem. Soc. Abstr.* 1921, ii. 112).

The heat of formation of sodium silicate has been determined from the interaction of sodium silicate and dilute hydrochloric acid, the following equation being obtained: Na_2SiO_3 (solid) + 2HCl (dissolved) = SiO_2 , aq. (precipitate) + $2\text{NaCl} + \text{H}_2\text{O} + 32.8$ cals., whence SiO_2 , aq. (precipitate) + $\text{Na}_2\text{O} = \text{Na}_2\text{SiO}_3 + 51.1$ cals.; SiO_2 , aq. (precipitate) + $\text{Na}_2\text{CO}_3 = \text{Na}_2\text{SiO}_3 + \text{CO}_2 - 24.7$ cals.; and Si (crystalline) + $3\text{O} + 2\text{Na} = \text{Na}_2\text{SiO}_3 + 331.4$ cals. (C. Matignon, *Bull. Soc. chim.* 1924, 35, 29; *J. Soc. Chem. Ind.* 1924, 43, B. 214).

Aqueous solutions of sodium silicate, even when diluted, are precipitated by alcohol. On treatment with acids, even carbonic acid, the salt may decompose with separation of gelatinous silica; the alkaline carbonates and chlorides, especially ammonium chloride, may also precipitate the silica. For the reactions between sodium silicate and ferric chloride solutions, *see* Liesegang (*J. pr. Chem.* 1913, [ii.] 83, 358; *Chem. Soc. Abstr.* 1913, ii. 861). The electrolysis of sodium silicate solutions, *see* Spencer and Proud (*Kolloid Zeitsch.* 1922, 31, 36; *Chem. Soc. Abstr.* 1922, ii. 611). Use for manufacture of sodium carbonate, *see* p. 175, col. 2; for methods of removing sodium silicate from Leblanc soda liquors, *see* p. 171, col. 1, (5) and (6). Salts of the alkaline earths give precipitates of insoluble double silicates.

Action of air on solutions of sodium silicate. Hugo Ditz (*J. pr. Chem.* 1916, [ii.] 92) regards the statement that the solution of a silicate of an alkali metal when exposed to air undergoes partial oxidation to a persilicate (Jordis, *Chem. Soc. Abstr.* 1914, ii. 200) as highly improbable. A solution of such a persilicate should actually contain the hydrolytic products, namely, a silicate and hydrogen peroxide, but the only evidence mentioned is the presence of a little free chlorine in the carbon dioxide liberated by hydrochloric acid. Such a result might be due to the presence of a little manganese as impurity in the silicate solution. However, the author (Ditz, also Ditz and Kanhänsler, *Chem.*

Soc. Abstr. 1913, ii. 958) has shown that after prolonged exposure to the air many alkaline substances are found to contain small quantities of nitrite and nitrate, and treatment with hydrochloric acid would give rise to nitrous fumes with the former, and, if the acid were concentrated, to chlorine with the latter. Experimental test has confirmed the possibility of this result with a solution of a silicate of an alkali metal, distinct traces of nitrite being present even after exposure for two days, the amount being very appreciable after three months. In the same period the quantity of nitrate formed was relatively small, whilst titanous acid failed to reveal any trace of hydrogen peroxide (*Chem. Soc. Abstr.* 1916, ii. 99).

Sodium silicate, solid; 'water-glass,' or 'soluble glass.' This substance usually approximates to the composition $\text{Na}_2\text{O} \cdot 4\text{SiO}_2$, and most probably consists of a solid anhydrous solution of the metasilicate Na_2SiO_3 in a larger quantity of silica. It is prepared on a large scale from sodium sulphate or carbonate and white sand or powdered quartz. Typical mixtures employed for the charge are given below, the coal being added to assist in the reduction of the carbonate or sulphate.

1	2
100 lbs. powdered quartz	100 lbs. powdered quartz
28 lbs. calcined sodium carbonate	60 lbs. calcined sodium sulphate
	15-20 lbs. coal
3	4
180 lbs. white sand	180 lbs. white sand
110 lbs. sodium sulphate	100 lbs. 50 p.c. sodium carbonate
10 lbs. coal	3 lbs. coal
5	6
100 lbs. sand	100 lbs. sand
56 lbs. sodium carbonate	70 lbs. Glauber's salt
	4 lbs. wood charcoal

The amount of coal necessary with the sodium sulphate is only that required to convert it into sodium sulphite, since this reacts readily on the silica, and further a deduction may be made for the smoke from the furnace gases.

The coal in the No. 4 sample is added to reduce the sodium sulphate in the low grade impure sodium carbonate there used. The coal added should not be sufficient to further reduce the sulphite to sulphide, as this hinders the formation of the silicate. The coal, charcoal or sawdust are well mixed with the sulphate, and the mixing is continued while the sand is added. A Siemen's regenerator furnace 10 ft. by 30 ft. will make about 22 tons of water-glass in 24 hours with a consumption of 5 tons of fuel. The formation from sodium sulphate is more difficult and slower than from sodium carbonate.

Before a new furnace is used for making sodium silicate, a charge of bottle glass should be made in it so as to subsequently protect the brickwork. The temperature required is about 1100° , and the time 5 to 8 hours. When the charge is fused a portion only is drawn from an upper tapping hole, and the furnace with its part charge of molten silicate is then recharged with fresh raw materials (*J. Soc. Chem. Ind.* 1913, 599).

Smaller reverberatory furnaces with ordinary firing are also used, but their output is much smaller, $1\frac{1}{4}$ tons per day, and their coal consumption much larger, $1\frac{1}{2}$ tons per day.

The run-off fused product after cooling is sometimes colourless, but usually has a brownish or greenish colour due to iron; it is broken up by a stone breaker, and ground by suitable machinery.

According to Maetz (Chem. Zeit. 1918, 42, 569-570, 582-583), in the manufacture of sodium silicate, Glauber salt is now generally used in place of sodium carbonate on account of its lower price, although a greater weight has to be used in addition to a quantity of coal as a reducing agent, whilst it has a more destructive action on the furnace walls than carbonate. The materials are used in the proportion of 100 parts of sand, 75 of Glauber salt, and 8 of coal. The finely ground mixture is fused at about 1500°C. in a tank furnace constructed of fire-brick, the bottom being cooled externally by air-ducts connected with the chimney. The furnace proper communicates with a second compartment by means of a hole at a distance from the bottom one-quarter the depth of the charge. The fused glass falling to the bottom of the furnace, flows into the second compartment, which may be separately heated to keep the water-glass molten, and is thence discharged into an iron vessel filled with water to cool it. The furnaces are fired with producer gas and may be worked on the recuperative or the regenerative system, the former being suitable for small plant with a daily output of 1500-5000 kilos., whilst for larger installations, up to 20,000 kilos. per day, the regenerative system is better. The solidified water-glass is broken up into fairly small particles, usually by means of hammers. It is not now generally ground in a ball mill, as the finely divided particles ball together during the extraction process, and then only dissolve with difficulty.

A water-glass known as 'double soluble glass,' and containing about equal proportions of sodium and potassium silicates, is prepared by using the proper quantities of potassium and sodium carbonates in place of sodium carbonate alone. It is said to give a thinner solution than either the potassium or sodium salt of corresponding strength.

A number of sodium silicate preparations have been made by Ordway (Amer. J. Sci. [ii.] 32, 162, 337; 33, 27, 35; 35, 35, 185).

Sodium silicate solution.—Water-glass is nearly insoluble in cold water, but dissolves completely, although slowly, in boiling water, the solubility decreasing as the percentage of silica in the substance increases (*cf.* Caven, J. Soc. Chem. Ind. 1918, 37, 63, T.). Silicates containing more alkali than corresponds with the composition $\text{Na}_2\text{O} \cdot 2\frac{1}{2}\text{SiO}_2$ are deliquescent, and too poor in silica to be applicable to the ordinary uses of water-glass (Ordway, Amer. J. Sci. [ii.] 35, 193).

Commercially the crushed or powdered water-glass is dissolved by long boiling with water, preferably under pressure. The resulting solution is allowed to clarify, and is then evaporated to 40°Bé. in iron pans. The small proportion of sulphide sometimes present from the reduction of the sulphate can be removed by adding a little copper scale or litharge when preparing the solution. 100 lbs. of the solid yield about 300 lbs. of a solution of 40°Bé. Maetz (*see above*) treats the broken glass in the dissolving

drums with steam at about 5 atmospheres pressure, whilst the drums rotate at about 6 revs. per minute, the solution process taking about 6 hours. The capacity of the drums should be in the proportion of 1 litre to 1 kilo. of dissolved glass, so that, the sp.gr. of the water-glass being 1.5, the drum is two-thirds full at the end of the process. A convenient capacity is 6000 litres. For each kilo. of solid glass about 1½-2 kilos. of steam is used. When solution is complete the product is run off into settling tanks and, after the mud has settled, passed through a filter-press. The clear water-glass so obtained generally has to be concentrated, this being carried out in a closed steam-jacketed vessel connected to a vacuum pump, the solution being stirred during concentration to obtain a homogeneous product (*see also* Caven, Chem. Zeit. 1918, 63 T.; J. Soc. Chem. Ind. 1919, 38, 72 A.).

Sodium silicate solution is largely prepared by a direct wet process on account of the greater uniformity of the product. It consists in digesting silica 2.8 parts—preferably infusorial earth—with a solution of caustic soda of sp.gr. 1.22-1.24 (prepared by causticising a solution of sodium carbonate with lime) containing 1 part of caustic soda, under three or four atmospheres pressure. The liquid is heated by blowing in steam, and is kept stirred by machinery. Complete solution is attained in about 3 hours, as shown by withdrawing a sample, when the suspended matter ought to settle rapidly and be of a brick-red colour (Fe_2O_3), whilst the liquid should be almost free from alkaline reaction. The caustic soda must not be above 1.24 sp.gr. as a stronger solution holds the fine sand and ferric oxide in suspension for a long time, such solutions not clarifying properly even after standing for several days. The clarified liquid is drawn off, it has a sp.gr. of about 1.18, the decrease being due to the dilution produced by the condensed steam. Instead of infusorial earth, other forms of silica, such as powdered flints, quartz, &c., can be employed, but the digestion must then be continued for a longer time and under 7-8 atmospheres pressure. The clear solution is then concentrated in iron to the required strength, usually 1.7 sp.gr.

A pure silicate may be made from the crude product by passing a current of carbon dioxide through the solution, filtering off the precipitated hydrated silica and redissolving it in caustic soda.

The aqueous solution of sp.gr. 1.7 usually has the following composition: silica 32-33 p.c., soda 16-16½ p.c., other sodium salts 2½-3 p.c., water 48-49 p.c.

The following is a list of patents dealing with the manufacture of water-glass:—

Ransome, Eng. Pats. 10360, 1844; 10665, 1845; 1666, 1853; 645, 1855; 2267, 1856. Kuhlmann, Eng. Pat. 367, 1853. Losh, Eng. Pat. 14208, 1852. Gossage, Eng. Pats. 762, 1854; 799, 1099, 1859. Kayser, Williams, and Young, Eng. Pat. 11493, 1887. Sievert, Eng. Pat. 4021, 1890. Crosfield and Markel, Eng. Pat. 18998, 1894. Garroway, Eng. Pat. 2489, 1896. I. J. Brown, Eng. Pat. 24237, 1902. Watson, Eng. Pat. 25394, 1904. Henkel, Eng. Pat. 23391, 1911. Spensley, Battersby and Holmes, Eng. Pats. 11959, 1914; 108576, 1917. Caven, Eng. Pats. 106247, 1917; 108372, 1917.

For new crystalline silicates of potassium and sodium, their preparation and general properties, *see* Morey (J. Amer. Chem. Soc. 1914, 36, 215; Chem. Soc. Abstr. 1914, ii. 202).

Applications.—Sodium silicate is largely used, on account of its detergent properties, as an addition to soap, principally to those intended for toilet use, as it imparts hardness and durability. Two typical analyses of such soaps are given below:—

	I.	II.
Soda	12 p.c.	12.5 p.c.
Silica	10 „	8.5 „
Water	30 „	33.0 „
Fatty acids . .	48 „	46.0 „

These soaps were first introduced by Gossage, and the sodium silicate solution was added to the soap just before the final cooling.

Silicates of the more silicious type aid soap in emulsification, and have slight emulsifying powers of their own against pure mineral oil; they emulsify saponifiable and impure unsaponifiable oils more readily (and the more alkaline silicates share in this property). An emulsifying agent composed of neutral soap and one of the higher ratio silicates is better than either soap alone or soap and sodium carbonate. Sodium silicate if not used in too great concentration stabilises a soap lather, and appears preferable to sodium carbonate in this respect. Laundry tests showed that a high ratio silicate, *e.g.* $\text{Na}_2\text{O}, 3.3\text{SiO}_2$, either alone or with soap, could be used to wash greasy overalls. It is concluded that the use of sodium silicate as a detergent in combination with soap is justified by reason of its effect on the emulsifying and lathering powers of the latter (A. S. Richardson, J. Ind. Eng. Chem. 1923, 15, 241–243; J. Soc. Chem. Ind. 1923, 42, 364 A.).

Solutions of sodium silicate are largely used as an adhesive for which it possesses all the essential properties, *viz.* (1) ease, suitability, flexibility, and general efficiency of application to the materials to be united, and (2) power of 'setting' in a suitable manner and time. Its viscosity can be adjusted to the purpose for which it is required. As an adhesive it does not putrify or decay and is immune from bacterial activity. It is cheap, odourless, and damp-proof, and can be applied cold. It is used to a large extent in the built-up paper-board industry, the production of multiply veneer, and in the manufacture of 'mandree' paper articles for food containers, packages, cartons, corrugated or crimped paper, &c. (Furness, J. Soc. Chem. Ind. 1922, 41, 381, R.).

On account of its glass-like nature and stability at high temperatures, water-glass enters into the composition of many fireproofing media. Wood may be painted with water-glass alone, or with a hot mixture of sodium silicate, glue, and Spanish white (chalk). For textiles, silica may be deposited by after treatment with dilute hydrochloric acid, followed by washing and heating; but this treatment imparts harshness to the fabric. A rubber emulsion, containing water-glass, borax, and a metal powder, has been suggested for waterproofing and fireproofing fine fabrics such as lace (Eng. Pat. 160627 of 1920). The adhesive properties of sodium silicate are turned to advantage both in coating

materials with solid fireproofing compositions and in the formation of fireproof masses containing steel wool, silicate cotton (slag wool), or asbestos. A fireproof coating of wool is made by treating solid sodium silicate (350 parts) an asbestos powder (350 parts) with boiling water (1000 parts); or the wood is first treated with a mixture of equal parts of magnesium silicate, sodium phosphate, and borax, and subsequently finished with water-glass (Fr. Pat. 472172 of 1914). A cement, for converting sheets of paper into fireproof pasteboard, consists of potash water-glass (5–10 p.c. free alkali) mixed with chalk (D. R. P. 298129 of 1916). Fireproof masses may be made by moulding a mixture of slag wool, filler and water-glass, followed by treatment with a solution of calcium chloride, while the structural material 'uralite' is made by spraying asbestos with a mixture of water-glass and sodium bicarbonate (Pharm. J. 1924, 112, 649).

Sodium silicate is largely used for impregnating sandstone and other porous stones as a protection against weathering. The stone is treated with a solution of water-glass, followed by the application of a solution of calcium chloride or aluminium sulphate, which causes the deposition of an insoluble silicate in the pores of the stone, greatly increasing its hardness and durability. The soluble sodium salt formed is removed by a subsequent washing (*see also* Burnell, J. Soc. Arts, 8, 240).

Aqueous solutions of aluminium chloride and sodium silicate react to form a precipitate of the composition $2\text{Al}_2\text{O}_3, 3\text{SiO}_2$, which adsorbs silica, and in presence of sufficient silicic acid is converted into the compound $\text{Al}_2\text{O}_3, 2\text{SiO}_2$, analogous to kaolin, $\text{Al}_2\text{O}_3, 2\text{SiO}_2, 2\text{H}_2\text{O}$. Investigations of the X-ray spectra of these products and of the course of their dehydration indicate that the first is amorphous, and that, under the conditions of experiment, one compound only, $\text{Al}_2\text{O}_3, 2\text{SiO}_2, x\text{H}_2\text{O}$, is formed (R. Schwarz and A. Brenner, Ber. 1923, 56, [B.] 1433).

An important application of water-glass is in the manufacture of artificial stone. The following is an outline of the process used at an English works for the manufacture of chimneys, pots, mouldings, &c. The sand or sandstone employed having been ground wet, and passed through a 40-mesh sieve is thoroughly dried and mixed in a revolving pan provided with scrapers and edge mixers with sufficient liquid water-glass to form a moist, coherent mass. It is then pressed into moulds and is saturated before removal with a solution of calcium chloride drawn through by a vacuum equal to about 20 ins. of mercury. Calcium silicate having thus been formed as above, the stones are transferred to boiling tanks heated by steam, and, after a sufficient time to complete the setting, are conveyed to washing tanks, in which they are subjected to the action of running water for a fortnight, to remove the whole of the sodium chloride.

Water-glass is also employed in the calico-printing and dyeing industries as a fixing agent for pigments; in printing indigo; as a resist for certain colours, and in the finishing of cotton goods. It is a constituent of certain lead-free enamels for glazing pans, &c., intended for domestic use, and is occasionally employed in

the basic linings of Bessemer converters. It is used in fixing fresco-painting (stereochromy), in bleaching jute, for preventing wood from rotting, and for preserving eggs. A mixture of 2 parts fluorspar and 1 part powdered glass made into a thick paste with water-glass is used as a cement for glass and porcelain.

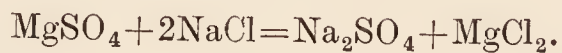
A multiplicity of uses for sodium silicate are described by Feuchtwanger in his 'Soluble Glass,' and also in Kane's Chemistry, p. 437. During the war period, 1914-18, it has been found that the most varied chemical plants may be constructed from blue bricks set in a mixture of ground firebrick and sodium silicate solution; Chance and Hunt (Eng. Pat. 110258, 1917; J. Soc. Chem. Ind. 36, 1237) give details for a cement that withstands the actions of all acids, chlorine, sulphuretted hydrogen, &c.

Sodium stannate. See under TIN.

Sodium sulphate Na_2SO_4 , technically called 'sulphate,' or 'salt-cake,' was first obtained by Glauber, by the decomposition of common salt by sulphuric acid and the crystallised sulphate containing 10 molecules of water of hydration, is still called 'Glauber's salts.' Both the anhydrous and the hydrated salts are found in many places in nature; the former, as a mineral, is called *thenardite*, m.p. 884.7° (H. S. Roberts, l.c.), the latter *mirabilite*. Large quantities of sodium sulphate occur native, especially in Spain, at Lodosa, in the Ebro valley, and elsewhere, and in the Western States of North America. The double sodium and calcium sulphate called *glaucoberite*, also occurs naturally in large quantities and in many places.

Sodium sulphate is frequently obtained as a by-product of other manufactures, of which we mention four.

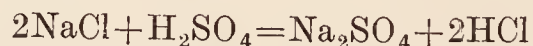
(1) From the (now almost obsolete) manufacture of hydrochloric acid in cast-iron cylinders from common salt and sulphuric acid; this product, called *cylinder-cake*, mostly contains from 7 to 10 p.c. of undecomposed sodium chloride. (2) From the preparation of nitric acid from sodium nitrate and sulphuric acid; it ('nitre-cake') always contains a considerable proportion of acid sodium sulphate NaHSO_4 . (3) From the residues ('Abraumsalz') left on dissolving the crude carnallite at Stassfurt. The latter contains a large quantity of insoluble *kieserite* $\text{MgSO}_4 \cdot \text{H}_2\text{O}$, which, on being exposed to the weather, or brought into contact with water for some time, gradually yields soluble magnesium sulphate $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$. The residues at the same time contain much common salt, and, if necessary, more of the latter is added, so as to bring up the quantity to the proportion of 2 NaCl to 1 MgSO_4 . When this mixture is dissolved in water and the solution is exposed to a natural or artificial cooling a few degrees below 0° , the following decomposition (noticed by Scheele as early as 1787) takes place:—



The sodium sulphate crystallises as Glauber's salts, the magnesium chloride remaining behind. Many thousands of tons of Glauber's salts are made at Stassfurt in this way. (4) By heating sulphides with common salt in the presence of air. From the extraction of copper and silver from certain sulphide ores and products by

mixing them with salt and roasting in the air whereby the salt is converted into sodium sulphate, but it was not commercially extractable. In 1842 Longmaid introduced a modification of this process, by which the sodium sulphate was to be obtained in a marketable form; but it was found in the working of Longmaid's process in several places over a number of years that the method was not commercially successful.

Glauber's process for the preparation of sodium sulphate



at present produces by far the larger part of the sodium sulphate used. We shall omit mention of the obsolete methods of performing this operation in glass retorts or iron cylinders, and describe the process as now carried out, first emphasising that owing to the regulations of the Alkali Acts for the condensation of acid vapours the manufacture is most intimately connected with the simultaneous manufacture of hydrochloric acid which imposes difficulties on the process; the article on Hydrochloric Acid under the heading of *Chlorine*, Vol. II. p. 216 to p. 221, should therefore be read.

The raw materials are:

1. *Sodium chloride*.—In England the grade of manufactured white salt called 'pan-salt' is generally used, being free from iron and containing only 1-2 p.c. of calcium sulphate, and being of a coarse grain which is of great advantage in the process; it contains 8 to 10 p.c. of water. Rock salt is also employed to a great extent; this must be coarsely crushed, not finely ground, and should be as free as possible from calcium sulphate and clay. The permissible impurities and their amounts depend on the purpose for which the salt-cake is afterwards to be used.

2. *Nitre-cake*—that is, the residue from the manufacture of nitric acid, consisting of a mixture of a normal and acid sodium sulphate. Nitre-cake is frequently mixed off with an ordinary charge of salt. The free acid determined by analysis replaces part of the sulphuric acid which would otherwise be required to decompose the salt used. The nitre-cake is broken into lumps which readily melt in the decomposing pan.

3. *Sulphuric acid*.—This should be neither too weak nor too strong, preferably about 140° —that is, at the strength it usually comes from the Glover tower. Stronger acid acts too rapidly, and yields badly mixed batches; weaker acid retards the operation and injures the pots.

The decomposition of NaCl by H_2SO_4 , though commencing at ordinary temperatures, is not completed until a dull red heat is attained. It is the usual practice, therefore, to divide the operation into two stages, the first of which is performed almost always in a cast-iron pot, the second in a brick furnace.

The two stages are generally expressed as:

1. $\text{H}_2\text{SO}_4 + 2\text{NaCl} = \text{NaHSO}_4 + \text{NaCl} + \text{HCl}$
at low temperatures.

2. $\text{NaHSO}_4 + \text{NaCl} = \text{Na}_2\text{SO}_4 + \text{HCl}$
at high temperatures.

In practice more than 50 p.c. of the reaction takes place in the first stage. The actual amount depends on the temperature of the

charge in the decomposing pan or pot, and varies from 65 to 75 p.c. of the whole.

The apparatus for the first or low temperature reaction.—The cast-iron pots, or *salt-cake pots* are now always made in the shape of shallow cast-iron dishes, 9 to 11 ft. in diameter, and 1 ft. 9 ins. to 2 ft. 6 ins. deep; the thickness of the metal varies from 5 to 7 ins. in the centre, and from 2 to 3 ins. at the sides. These 'pots' weigh from 5 to 6½ tons, and must be made of a special mixture, so as to combine resistance to chemical action with toughness and resistance

to changes of temperature. Their edge is sometimes quite plain, sometimes provided with an ordinary horizontal flange; but, best of all, with an upstanding margin on a horizontal flange, as shown on the right side in Figs. 54 and 55, from which the covering dome of brickwork is sprung, so that any leak occurring here cannot cause the escape of hydrochloric acid into the fire-flues. The dome is built of acid-resisting brick, usually set in a mixture of salt and mortar. The common method of building the dome is to fill the pot with salt and then heap on more salt

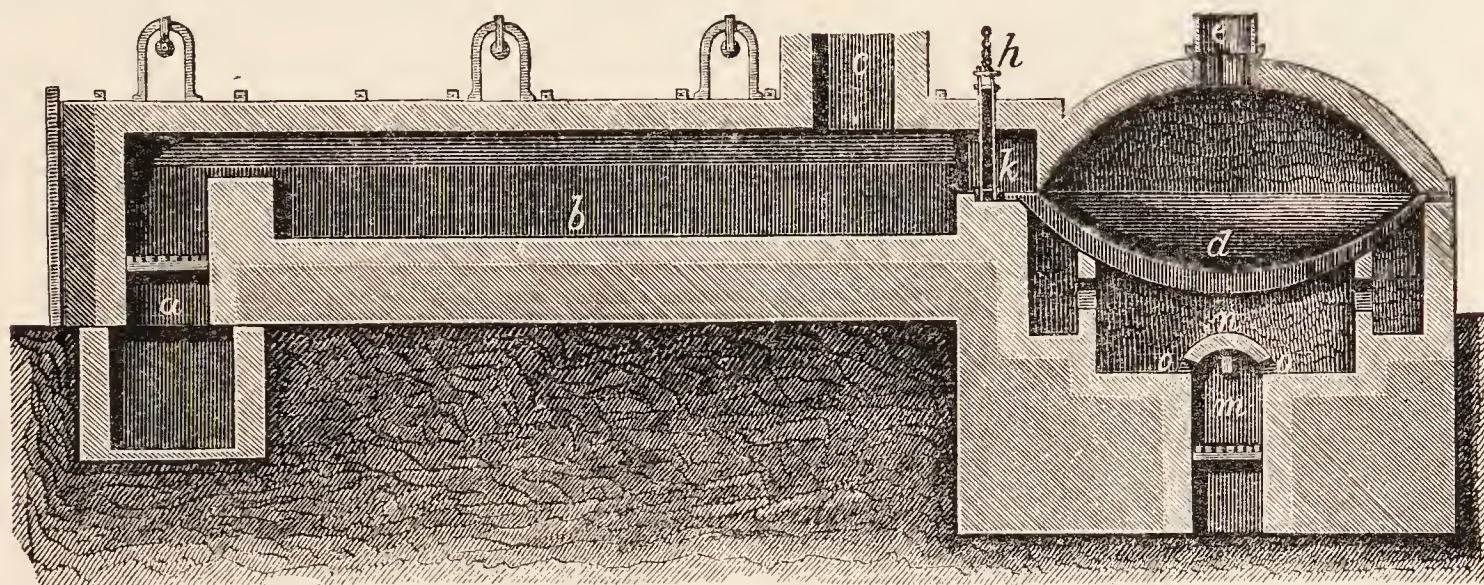


FIG. 54.

until a mound of salt is obtained of the desired shape, and the dome is then built on the mound of salt as the centering. The arrangement of baffles over the fire and under the pan (see Fig. 54) is for the purpose of equally distributing the heat; the exit pipe for the strong hydrochloric acid gas is *e*. In Fig. 55 the working door is shown in the front.

Near the decomposing-pan there must be a cistern for measuring the sulphuric acid to be run in for each charge (this is not shown in the figures). It is preferable that this acid should

be moderately warm, and this can be attained by employing as gauge-vessel an iron pan lined with lead, and placing this over a hot flue.

The sulphuric acid from the gauge-vessel is run into the pan through a luted lead pipe which passes through the dome and delivers a slow stream of acid on the salt in the centre of the pan.

The apparatus for the second, or high temperature reaction.—The brick furnace, called the roaster furnace, used to have the form of a reverberatory furnace, as shown in Figs. 54 and

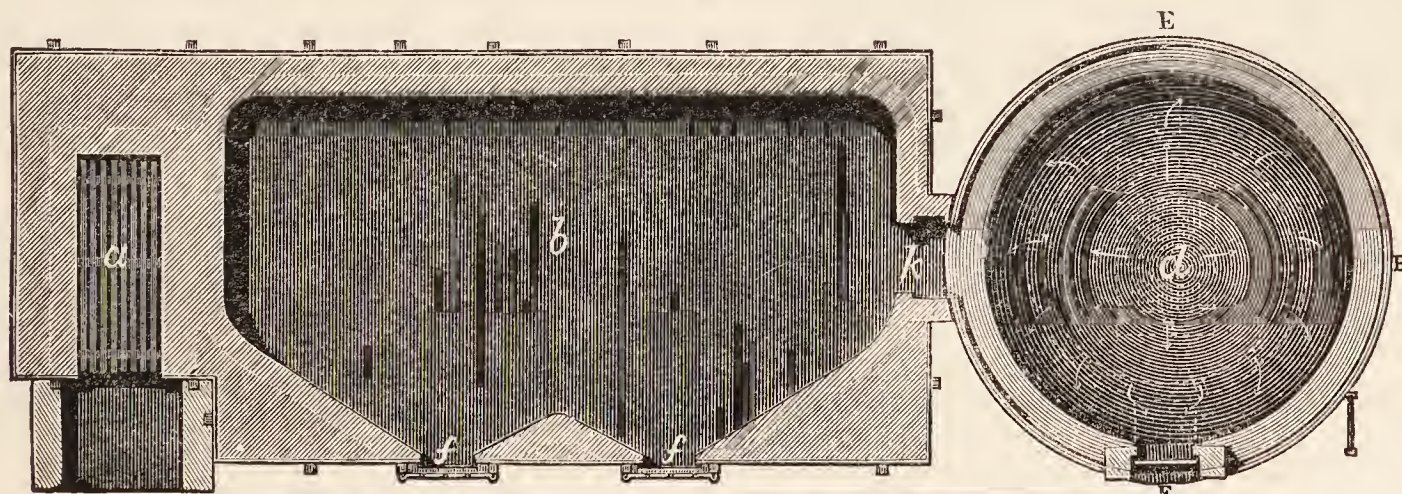


FIG. 55.

55, on the left side, but these have now nearly all disappeared owing to the difficulties and expense of efficiently cooling and condensing the hydrochloric acid gas produced in the roaster, owing to its being mixed with such large volumes of the products of combustion from the fireplace.

This trouble with the condensation of the acid gas led to the replacement of the reverberatory brick finishing furnace by a muffle brick finishing furnace or closed furnace, although these last are more difficult to construct and more costly to repair.

In the early days of the muffle salt-cake furnaces very considerable difficulties were experienced in keeping the muffle arch sufficiently tight to prevent leakage of the HCl from inside the muffle into the chimney flue. This was not only a source of loss of HCl, but was liable at any time to cause an infringement of the British Alkali Acts, which specify a maximum HCl content of the chimney gases of 0.2 gm. HCl per cubic foot.

To meet this difficulty suggestions were made by Muspratt and by Gamble of means to place the flue gases under a higher pressure than the

gases inside the muffle, and thus to cause any leakage which might take place to be from the fire-gas flue into the muffle. In 1876 Deacon brought out this 'plus pressure' salt-cake furnace which bears his name, and which is to-day by far the most extensively used of all the hand salt-cake furnaces (Figs. 56, 57, 58, and 59).

The plan adopted by Deacon was extremely ingenious, and consisted in building the fire-place on a considerably lower level than the

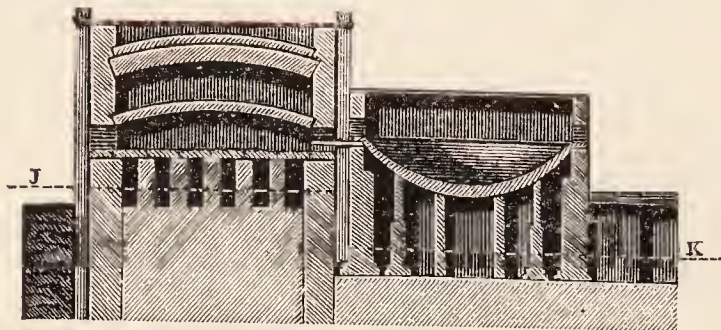


FIG. 56.

muffle and its furnace (see Fig. 57), and utilising the comparative pressure produced at the top of the lengthened vertical column of hot specifically light flue gases to overbalance the gaseous pressure inside the muffle.

Fig. 57 shows a sectional line LM which passes longitudinally right through the centre of the muffle; above this line are two partitions, first the top of the muffle, and above that the top of the furnace, above which are the tie-rods holding together the cast-iron buck stays to strengthen the brickwork; the fire flue is the space between these two partitions and the gases pass from left to right, they then descend by a flue (which is also shown by Fig. 58 on the right) and pass under

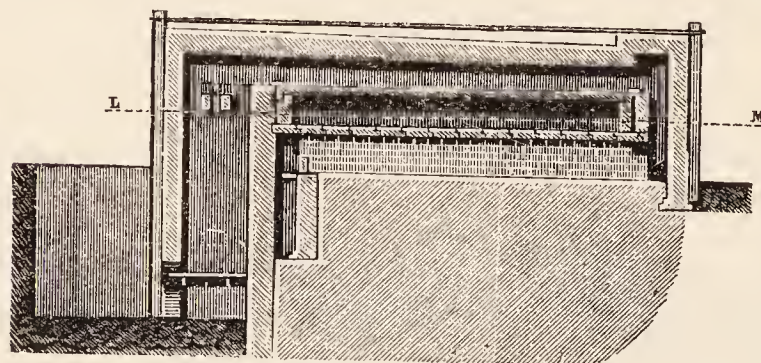


FIG. 57.

the muffle by six parallel flues (Figs. 56 and 59) formed by the tiles constituting the bottom of the muffle (Fig. 57), the side walls of the furnace and five additional low-walls, and the ground. Fig. 56 is a cross-sectional elevation, and shows the way in which the bottom of the muffle is supported on the five low walls and the long sides of the furnace, and how the top of the muffle and the top of the furnace are each supported by arching them. The fire gases then collect together (Figs. 57 and 59), and leave the muffle by a flue shown only by Fig. 59, and so reach the flues under the pan; Fig. 59 is the flue plan as seen below the dotted line JK in Fig. 56. The charging hole, and the shoving hole for the pan, and one of the discharging holes for the muffle are shown in Fig. 56; the shoving hole and three discharging holes for the muffle are shown in Fig. 58. With due attention to all details a salt-cake pan will produce up to 4000 tons of salt-cake before it is corroded through or cracked.

The processes.—In this country a batch of

salt is up to 18 cwts., on the Continent it is smaller; the time required to work each batch is 2 hours. A small quantity of the charge of salt is thrown into the pan, and the sulphuric acid, preferably heated to some extent, is started running in; the rest of the salt is then thrown in as quickly as possible. The quantity of the acid must, of course, be exactly regulated to the weight and purity of the damp salt used, and in measuring it in the gauge-vessel, the volume and the hydrometric strength, and also the temperature of the acid must be observed and the tables employed that are given in *The Technical Chemist's Handbook*, by Lunge.

About 2-3 p.c. more acid is employed because sulphuric acid or anhydride is volatilised, especially in the roaster. Whether the proportions employed have been correct or not must be decided in each particular case by testing the salt-cake, which ought not to contain more than 0.5 p.c. undecomposed salt, or above 1 p.c. free acid (calculated as SO_3).

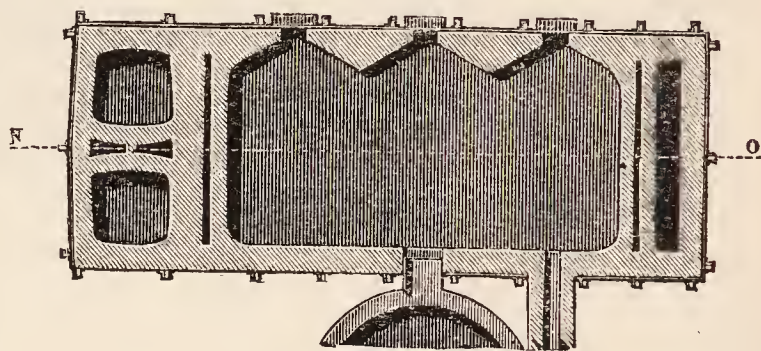


FIG. 58.

The first reaction between the ingredients in the salt-cake pot is very violent, and there is a tendency for the mass to rise and to froth over, which is counteracted by throwing in a little tallow. The salt should be dissolved in the vitriol, which is easily done with common pan-salt, but much less easily with rock salt, and is assisted by occasional stirring, the rake handle passing through a slot in the charging door. The fire is then increased to drive off more hydrochloric acid (but not too much, lest the batch becomes too stiff), and the batch is thoroughly turned over and mixed; the work is regulated in

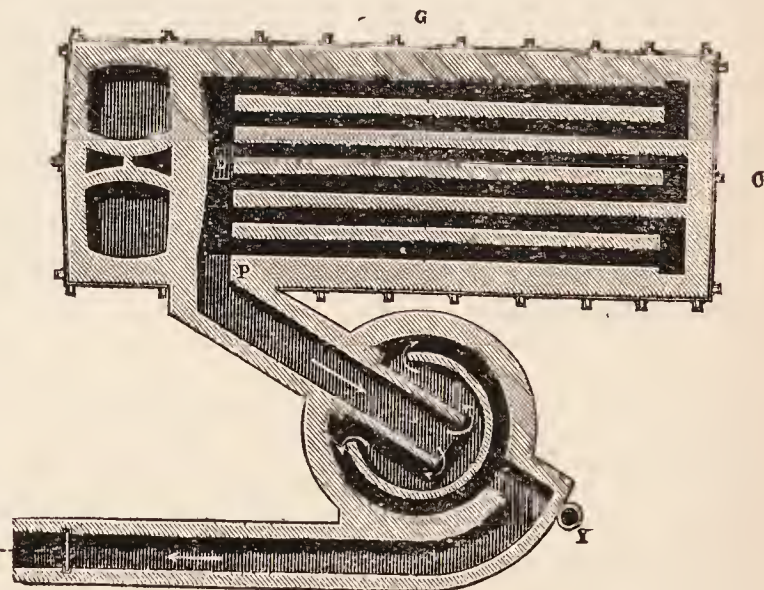


FIG. 59.

such manner that the batch is ready to be 'cast' or 'shoved' into the roaster, just when the last charge has been drawn from the latter.

The temperature within the roaster furnace should ultimately be a red heat, and then no

more vapours should be seen rising from the mass. Still, it usually happens that, on drawing the batch out of the furnace, gases are given off (those of sulphuric anhydride being less pungent than those of hydrogen chloride), and, to avoid nuisance, the mass is frequently first drawn into a closed box, where it cools down and is then removed without causing inconvenience.

The yield of salt-cake is very nearly that calculated by theory.

The consumption of fuel varies from 30 to 50 parts to 100 of salt-cake.

Mechanical salt-cake furnaces have been constructed by many inventors to economise labour and coals. We mention among such furnaces those of Jones and Walsh (1875; improved in 1887; cf. Chem. News, 35, 51); Cammack and Walker (1876); Black and Hill (1877); Mactear (1879) described J. Soc. Chem. Ind. 1881, 29, and shown in Fig. 60; Black and Larkin (1884); A. Walker (Eng. Pat. 9760 of 1887); Thomson and Worsley (Eng. Pats. 21945 and 21946, 1894).

Mactear's furnace has been the most successful. It consists of a revolving circular bed, covered by a fixed arch, the fire passing between them, and the access of air being prevented by a

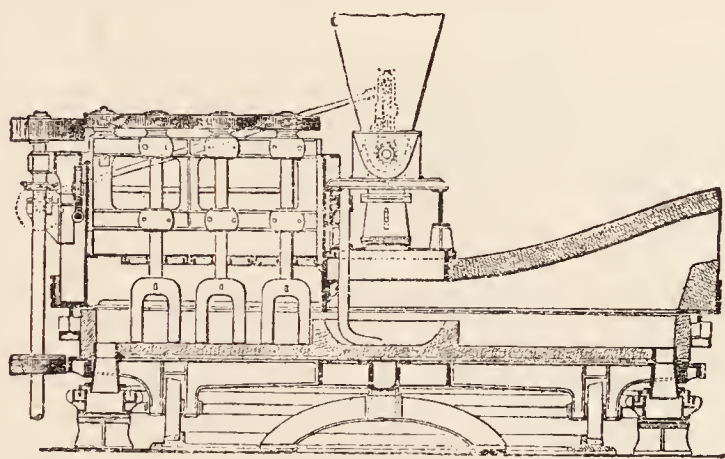


FIG. 60.

'lute' filled with crushed salt-cake. In the centre there is a kind of pot into which both salt and acid are continuously fed, and in which they are mixed. The pasty mass overflows into the outer beds, and is both continually stirred and gradually carried to the outer circumference by means of a number of stirrers, which are protected against the action of the fire and the acid gases by being placed between the gas-flues. The finished salt-cake, arriving at the outer edge, falls into the delivery trough running all round the furnace, and at the same time forming another 'lute.' The acid vapours and products of combustion pass away together in two flues, arranged at each side of the row of stirrers. The bed of the furnace is lined with fire-brick, boiled in tar and set in a special cement, which becomes harder when subjected to the action of the heat and sulphate. A great point in the Mactear furnace is that a continuous and even stream of hydrochloric acid is evolved, and, although this is mixed with all the fire-gases, it was claimed that the condensing-plant required is decidedly less than that found necessary with close furnaces. This claim, however, is not in agreement with practice.

The Mactear furnace was first fired with coke; then 'Wilson' producers were attached to it, but these have had to be given up again for coke.

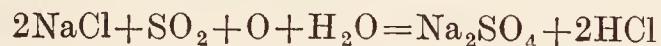
The Black and Larkin furnace, which is combined with an ordinary pan, is a peculiarly constructed muffle, heated from without by a number of small fires, both above and below, practically on the 'plus-pressure' system, with a very efficient mechanical stirring apparatus, thus permitting all the work to be done with closed doors, and avoiding 'low-level escapes.' Naturally the condensation of the hydrochloric acid is as easy in this case as with ordinary close roasters. One such furnace decomposes from 72 to 80 tons of salt per week. These furnaces have been successful, and are still at work in the place where they were originally introduced.

Walker's furnace consists of two revolving cylinders.

Though mechanical salt-cake furnaces have been used for so many years and have absorbed much skill and patience in their design, they have not been generally adopted, owing to their higher first cost, higher cost of repairs, and the difficulties of condensation of the hydrochloric acid gas more than balancing their undoubted economy in labour and capability of producing a more uniform salt-cake.

Hargreaves' and Robinson's process for manufacturing sodium sulphate from common salt, sulphurous acid, and air.—This process, which avoids the use of sulphuric acid, has been the subject of many efforts, commencing with Gossage's, in 1850. None of these had any practical success until Hargreaves and Robinson (beginning from 1870) introduced a number of improvements which have made that process practicable and successful. We shall here describe it in its improved form.

The process consists in conducting the gases from pyrites kilns of the usual type, mixed with a suitable quantity of steam, through a series of large cast-iron cylinders, charged with common salt, in such manner that the fresh gas meets with the salt which has been the longest time exposed to the treatment, whilst the nearly-exhausted gas is brought into contact with fresh common salt. In this way, on the one hand, the salt is completely converted into sulphate, and, on the other hand, the pyrites kiln gases are nearly as fully utilised as they would have been by passing them into vitriol-chambers. The reaction:



takes place at a temperature of about 500°–550°C., and this must be maintained against the radiation into the surrounding space by external heating; but as the reaction itself produces heat, the amount of fuel required is not excessive if care is taken to avoid undue loss of heat during the process. This is all the more necessary, as the process is a slow one: it takes from 2 to 4 weeks before the salt, charged into one of the cylinders, can be taken out in the shape of finished salt-cake.

The first step is bringing the salt into such a condition that the gases can readily pass through it and yet reach all parts of it to the very core. Salt of fine grain must be used, and usually either the salt known as 'butter salt' or powdered rock salt, or a mixture of both, is taken. A method of preparation generally adopted is as follows: The salt is crushed and moistened by water or exhaust steam. It then falls from a

hopper upon an endless chain of plates, each about 12 ins. broad and 5 ft. across, of a total length of about 100 ft. or more, rising up in a sloping oven and returning underneath. On falling upon that travelling-platform, the salt is mechanically beaten down into a layer of 1–1½ in. thickness, which is at once cut, by means of mechanically-moved knives, into cakes about 3½ ins. square. These now enter into an oven (heated by the waste heat of the cylinder jackets or by direct fire), and pass through it at such a rate that they arrive perfectly dry at the upper end. As the chain turns downwards the dry cakes detach themselves and fall down upon a grating. They are now dense enough to retain their shape in the cylinders, and to be handled without formation of any material quantity of dust, and yet porous enough to be entirely penetrated by the gases, their regularity of shape securing regularity of draught in the process. It is of vital importance that uncaked or powdery salt shall not get into the cylinders, as if it does, it forms areas impermeable to the flow of the gases, and thus prevents the reaction from being completed.

The decomposition of the salt takes place in

a series of cylinders, from 8 to 20 in number, about 15 ft. in diameter, and 12 ft. high, each holding 40 tons of salt-cake at least, eight of

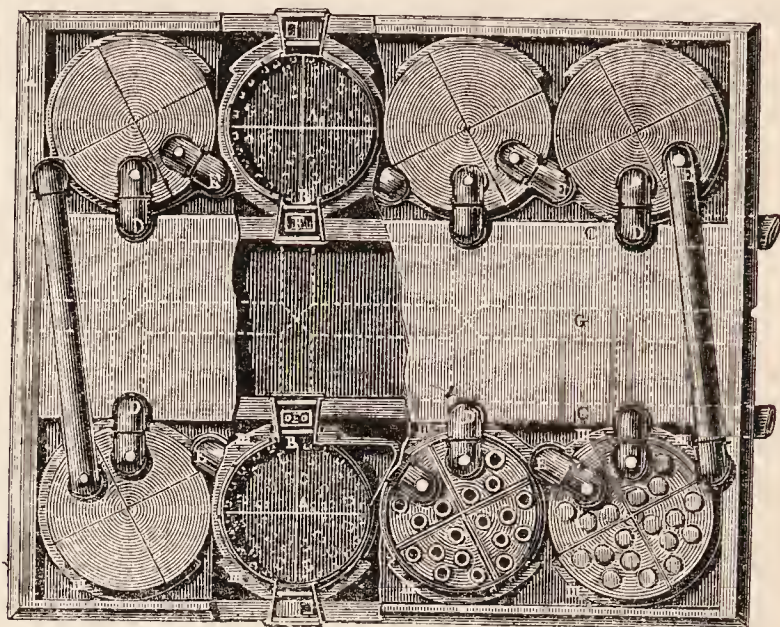


FIG. 61.

which are shown in plan in Fig. 61, while Fig. 62 shows on a larger scale a cross-sectional elevation of the group on a zigzag line passing

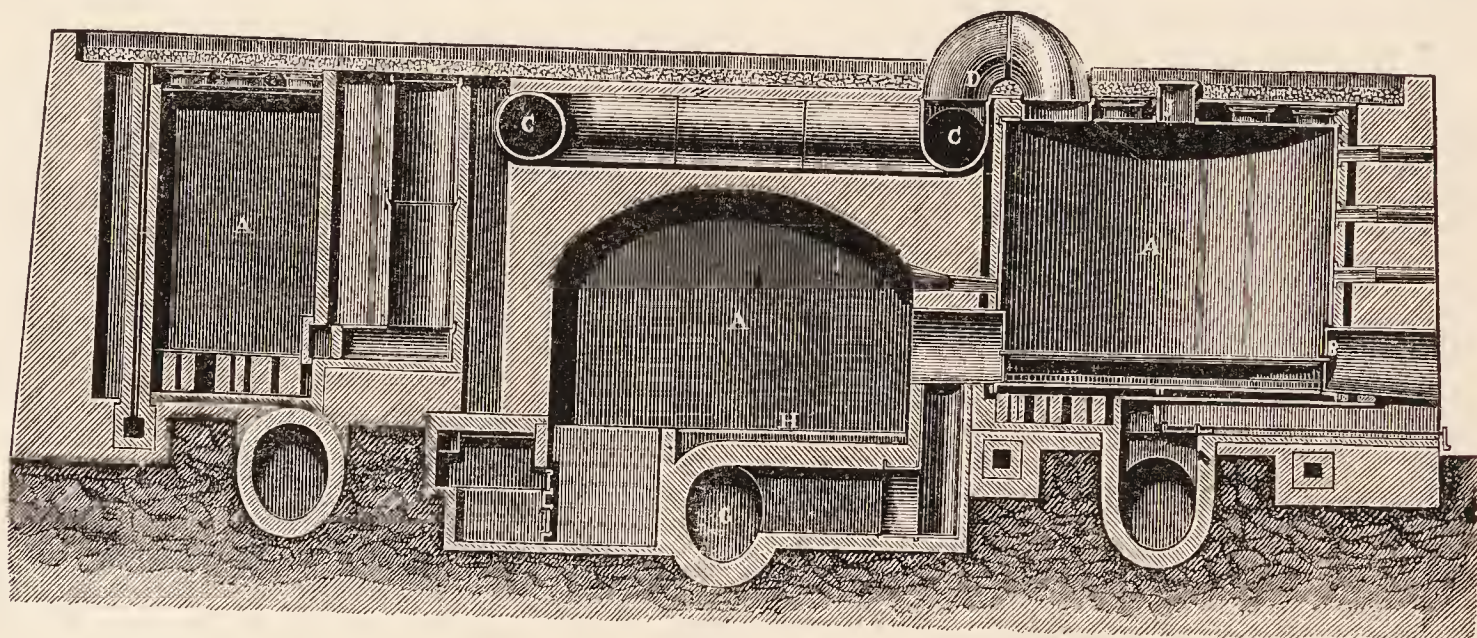


FIG. 62.

between two cylinders on its left, and through one cylinder A on its right side. The cylinders are surrounded by small vertical flues connected with a fireplace below, and their tops are closed by a cover plate that is protected against cooling by a thick layer of ashes, confined by the surrounding brick parapet (Fig. 62, top). Inside there is a removable grate, on which the salt rests (Fig. 61, the part in low section, and Fig. 62, right-hand A). A number of holes in the top serve for charging (see Figs. 61 and 62); a large door above the bottom serves for discharging (B, Fig. 62, right side). A set of large cast-iron pipes (CC in both figures) serves to admit the burner-gas into any one of those cylinders and for passing the residual gas through the whole series, the gas always entering at the top and going away at the bottom. The connections between the main gaspipe and any one cylinder and those between the single cylinders are opened or closed by a very simple arrangement known as a plate valve in the middle of the connecting pipes or 'siphons' (DD in both figures); the plate is luted with a mixture of mortar and salt to the two adjacent pipe ends and so effectively shuts the

connecting pipe; but if the plate is pulled away and the small remaining gap is luted up again then the connecting pipe is effectively opened. From the last cylinder of the series the gases pass through an opening in the bottom of the drawing doorway (Fig. 62, right) into a flue (G in both figures); J is an opening in the top by which cold air can be admitted, in case the cylinders get too hot through the heat of reaction.

The pyrites burners employed are specially constructed with a view to avoiding radiation, thus sending the gas as hot as possible into the cylinders. The necessary steam is superheated by the waste heat of the gases, and is usually introduced in the upper part of the burners.

The gases are drawn through the whole system by means of a Root's Blower or a cast-iron fan placed between the cylinders and the acid condensers. By keeping the blower so hot that no liquid acid can be condensed in it, it is protected against the action of the acid; but the ends of the shaft, passing through the blower, must, on the outside, run in water-cooled bearings. The exhaust steam of the engine is utilised

for the steam required for mixing with the burner-gas.

The amount of fuel needed in a special case was as follows (calculated upon 20 cwts. of salt-cake) :

For heating cylinders . . .	4	cwts.
For preparing salt . . .	3	"
For steam . . .	0.75	cwt.
	<hr/>	
	7.75	cwts.

In other cases nearly 10 cwts. of fuel has been required, but in any case no more fuel is needed than in the ordinary process of making sulphuric acid and employing this for decomposing the salt. The amount of fuel required for heating the cylinders depends naturally on the construction of the plant, the care taken to avoid radiation losses and to get the pyrites gases as hot as possible into the leading cylinders. It also depends on the rate at which the plant is working. The more rapidly heat is generated in the cylinders the less will be the proportion of that heat lost by radiation. The chemical composition of the salt has been held to materially affect the possible speed of working, and the evidence goes to show that other things being equal the salt containing the largest quantity of iron salts decomposes the most rapidly. This is the usually accepted explanation of the fact that the output of the same plant using powdered rock salt is greater than when using 'butter salt' which contains materially less iron.

Hargreaves (Fr. Pat. 384144, 1907) promotes the reaction by the addition of 0.1–1.0 p.c. of copper or iron salts before moulding into cakes, the amount used depending on the purity of the product required.

In large well-designed plants when the speed of reaction is high no fuel is required to heat the cylinders. Great care is necessary in watching and controlling the temperature of the Hargreaves cylinders. If the cylinders containing almost untouched salt get too hot through the rapid action of strong hot sulphurous acid gases, the salt itself will flux and form areas through which the gases cannot penetrate to complete the reaction.

The advantages of the Hargreaves process are a great saving in space and either, (1) when making the same quality of salt-cake lower process costs than the sulphuric acid and salt process, or (2) the power to make a higher grade salt-cake more free from iron than is possible in the ordinary process with the cast-iron decomposing-pan. The disadvantages are the great cost of the plant, which, unlike the lead vitriol chambers, does not return a large proportion of the initial on dismantling; the very careful supervision required with the consequent liability to serious difficulty and expense if the supervision even for a short time breaks down; and again the impossibility of utilising the hydrochloric acid gases evolved for the production of chlorine by the Deacon-chlorine process, Vol. II. p. 191, col. 2 to p. 193, owing to the quantity of sulphur dioxide and carbon dioxide they contain from time to time. This sulphur dioxide in the Deacon decomposers is fatal to the activity of the catalyst there used, viz. cupric chloride. The Hargreaves process is worked successfully in England in several manu-

factories, and also on the Continent, but has failed to extend materially in recent years.

Sodium sulphate free from iron (or nearly so) is required especially for plate-glass, window-glass, &c. The Hargreaves sulphate is frequently pure enough for this purpose. On the Continent it is sometimes made by employing decomposing-pans made of lead, which are certainly much more difficult to manage than the cast-iron pots otherwise used. The batch must be taken out much thinner, and the firing must be much more careful than with cast-iron pots.

Sodium sulphate from the native salt.—Anhydrous sodium sulphate is manufactured from natural salt deposits at Valmont, New Mexico.

Purified sodium sulphate is made by dissolving ordinary salt-cake, precipitating the iron present by the addition of a little bleaching powder and lime, and evaporating to dryness.

Testing of sodium sulphate.—It is usual in the factory to test the salt-cake only for free sulphuric acid and undecomposed sodium chloride, as these are the impurities over which the workman has control; the other impurities—iron, lime, alumina, &c.—depend on the quality of the salt used.

The usual methods of analysis adopted are given in Lunge's Technical Chemist's Handbook.

Two characteristic analyses of salt-cake are given below.

	Hand furnace salt-cake from white salt	Hargreaves salt-cake low in iron
Na_2SO_4 . . .	96.2	98.0
NaCl . . .	0.5	0.2
H_2SO_4 . . .	1.5	0.3
CaSO_4 . . .	1.8	1.424
Fe_2O_3 . . .	—	0.076
	<hr/>	
	100.0	100.0

Applications of sodium sulphate.—The chief use was for the manufacture of sodium carbonate, see p. 160, col. 2, and of caustic soda, see p. 214, col. 1, by the Leblanc process. It is largely used for the manufacture of sodium sulphide, and of glass. For the manufacture of practically all qualities of glass except lead glass, salt-cake is superior to soda ash because it is cheaper per unit of alkali, and owing to the higher temperature at which the glass furnaces work when using salt-cake a higher proportion of silica can be used, thus again cheapening the cost and also producing a harder and more durable glass. For its use for preparing copper carbonate and sulphate, see Vol. II. 371. For the molecular weight of anhydrous sodium sulphate, see Richards and Hoover (J. Amer. Chem. Soc. 1915; Chem. Soc. Abstr. 1915, ii. 96).

Properties Na_2SO_4 (anhydrous).—Crystallises in rhombic forms with a sp.gr. of 2.655. Heated, it suffers a transition at 233° to another form (see Landolt Bornstein Tables, 4th ed. 222; see also Jänecke, Zeitsch. physikal. Chem. 1916, 91, 548; Chem. Soc. Abstr. 1916, ii. 551, and 1917, ii. 15). The cryoscopy of sodium sulphate, see Leenhardt and Boutarie (Bull. Soc. chim. 1913, [iv.] 13, 651; Chem. Soc. Abstr. 1913, ii. 669). At 884° it melts and then has the sp.gr.

2.065—0.00045($t-900^\circ$)

Glauber's salt $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$. It is manufactured for a few purposes, principally for medicinal use and for freezing mixtures. A considerable quantity is obtained from the residuals of the Stassfurt salts, and from the mother-liquor in the manufacture of sea-salt. It is required in two very different states—viz. in very small or in large crystals. The small acicular crystals are obtained by making the solution as strong as possible at a temperature of 34°C ., settling, running into shallow coolers, and stirring the solution until it has cooled down. The larger crystals ('soda fashion') are made by dissolving the sulphate at 50° , until the sp.gr. is 1.257 (at 40°), settling for an hour, and running into deep coolers (2–5 ft. deep), where the liquor is kept quite undisturbed. In order to facilitate the formation of large crystals, wooden staves or pieces of twine, weighted with a little lead, are hung in the vats. The cooling lasts from 5 to 20 days, according to the size of the vats and the season, the crystals are large (an inch and more thick), hard and shining, and they must be dried at a temperature not exceeding 30° , to prevent efflorescing. The crystals are monoclinic; their sp.gr. 1.462; in the open air they easily begin to lose water and turn white; heated to 32.4° they melt and are converted into a mixture of the crystalline anhydrous salt, and a solution, and this mixture exposed to the air loses all water at just below 100° . According to Carles (J. Pharm. Chim. 1916, [vii.] 13, 219) officinal sodium sulphate is liable to contain arsenic which is present in certain samples of sodium sulphate, and the author suggests a modification of Marsh's test for detecting its presence. The issuing gas from the hydrogen generator is passed over a paper moistened with a solution of mercuric chloride, and after the purity of the hydrogen has been ascertained, about 25 grms. of the salt under examination are placed in the hydrogen-generating apparatus. The formation of a yellow or brown stain on the paper indicates the presence of arsenic, the depth of the colour giving an approximate measure of the amount present (Chem. Soc. Abstr. 1916, ii. 266). For the mixed crystals of sodium chromate and sodium sulphate, see Richards and Meldrum (J. Amer. Chem. Soc. 1921, 43, 1543; Chem. Soc. Abstr. 1922, ii. 54). For the action of oxalic crystalline acid on sodium sulphate, see Kohn-Abrest (Ann. Falsif. 1916, 9, 68; Chem. Soc. Abstr. 1916, i. 368).

The action of sodium sulphate on wool, see Fort (J. Soc. Dyers, 1913, 29, 80; Chem. Soc. Abstr. 1913, ii. 311). See also for the action of sodium sulphate on the dyeing of wool, Herz and Barraclough (J. Soc. Dyers, 1914, 30, 135; Chem. Soc. Abstr. 1914, ii. 346). The influence of sodium sulphate on plants, see Haselhoff (Chem. Soc. Abstr. 1913, i. 1425). The action of alcohol on the sulphates of sodium, see Butler and Dunncliff (Chem. Soc. Trans. 1920, 649). The light absorption of an aqueous solution of sodium sulphate, see Hulbert and Hutchinson (J. Phys. Chem. 1917, 21, 534; J. Chem. Soc. Abstr. 1917, ii. 557).

Heptahydrate $\text{Na}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$ is obtained when a strong solution, such as that obtained by melting the decahydrate as above, is cooled to 12° , or if weaker then to lower temperatures.

Solutions.—For solution the decahydrate requires at

	0°	18°	25°	32°	33°	50.4°
parts of water	8.22	2.08	1.00	0.37	0.31	0.38
The sp.gr. $18^\circ/4^\circ$ of	5 p.c.	10 p.c.	15 p.c.	20 p.c.		
is	1.045	1.091	1.142	1.138		

and the variations of the volume of these solutions with temperature may be found in Landolt Bornstein Tables, 4th ed. 289; see also Wuite (Zeitsch. physikal. Chem. 1914, 86, 349; Chem. Soc. Abstr. 1914, ii. 203). For the specific gravity and coefficients of dilation of solutions of sodium sulphate, see Tschernaj (J. Russ. Phys. Chem. Soc. 1914, 46, 8; Chem. Soc. Abstr. 1914, ii. 362). The aqueous pressure of crystals of sodium sulphate, see Baxter and Lanseng (J. Amer. Chem. Soc. 1920, 42, 419; Chem. Soc. Abstr. 1920, ii. 286). The solubility of anhydrous sodium sulphate in water, see Wilber (J. Phys. Chem. 1913, 17, 556; Chem. Soc. Abstr. 1913, ii. 672). See Richards and Yngve (Chem. Soc. Abstr. 1918, ii. 58) for the solubility of sodium sulphate as a means of measuring temperatures.

Sodium sulphate double salts.—Among the many double salts known are $\text{Na}_2\text{SO}_4 \cdot \text{CaSO}_4$ and $2\text{Na}_2\text{SO}_4 \cdot \text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, see Vol. I. 751; sodium alum $\text{Na}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$, see Vol. I. 179; sodium chrome alum, see Vol. II. 239. The double salt of potassium sulphate and sodium sulphate, see Okada (Chem. Soc. Abstr. 1915, ii. 344). The double sulphate of sodium and ammonium, see Matignon and Meyer (Compt. rend. 1918, 166, 686; Chem. Soc. Abstr. 1918, ii. 198); Gadolinium sodium sulphate, see Bissell and James (J. Amer. Chem. Soc. 1916, 38, 873; Chem. Soc. Abstr. 1916, ii. 330). For acid sulphates and pyrosulphates of sodium, potassium, and ammonium, see D'Ans (Zeitsch. anorg. Chem. 1913, 80, 235; Chem. Soc. Abstr. 1913, ii. 485). The double sulphates of samarium with sodium and ammonium, see Keyes and James (J. Amer. Chem. Soc. 1914, 36, 634; Chem. Soc. Abstr. 1914, ii. 370); yttrium sodium sulphate, see James and Holden (J. Amer. Chem. Soc. 1913, 35, 559; Chem. Soc. Abstr. 1913, ii. 508).

Normal and acid sulphates, see Pascal and Ero (Bull. Soc. chim. 1919, [iv.] 25, 35; Chem. Soc. Abstr. 1919, ii. 154). For the equilibrium of normal and acid sulphates, see Pascal (Compt. rend. 1917, 164, 628; Chem. Soc. Abstr. 1917, ii. 248). The equilibrium conditions for the manufacture of ammonium sulphate from sodium sulphate, see Nishizawa (J. Chem. Ind. Tokyo, 1920, 23, 25; Chem. Soc. Abstr. 1920, ii. 687). The equilibrium of ammonium sulphate, water and sodium sulphate, see Dawson (Chem. Soc. Trans. 1918, 675; Chem. Soc. Abstr. 1918, ii. 363); Matignon and Meyer (Chem. Soc. Abstr. 1918, ii. 66, 67, 302). For the compound of sodium sulphate with cadmium sulphate, see Calgagni and Marotta (Atti R. Accad. Lincei, 1913, [v.] 22, ii. 373; Chem. Soc. Abstr. 1914, ii. 52, 295). See also Art. CADMIUM, Vol. I. p. 732. The compound sodium sulphate with cobaltous sulphate, see Calgagni and Marotta (Gazz. chim. ital. 1913, 43, ii. 380; Chem. Soc. Abstr. 1913, ii. 1060).

Sodium bisulphate NaHSO_4 .—Obtained from a mixture of Na_2SO_4 and sulphuric acid, it forms at a dull red heat a clear product which solidifies to a mass of sp.gr. = 2.742; by

dissolving this in twice its weight of water and crystallising while warm, it is obtained as $\text{NaHSO}_4 \cdot \text{H}_2\text{O}$; if cold solutions are brought to crystallisation then the compound is decomposed and only neutral Glauber's salt is obtained. The anhydrous salt is the first product formed when preparing sodium sulphate from either salt NaCl (p. 250, col. 2), or Chile nitre NaNO_3 , and it is because of this that the second stages of those reactions have to be carried on at increasing temperatures. In the laboratory the fused salt is used for bringing insoluble oxides into the form of sulphates.

Sodium sulphides, monosulphide Na_2S , monosulphide hydrate $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$, monosulphide lower hydrates, disulphide Na_2S_2 , tetrasulphide Na_2S_4 ; other polysulphides, and analytical methods.

Sodium sulphide Na_2S . Commercially this compound is always obtained by the reduction of sodium sulphate. The preparation has been the subject of much work and many patents. Arrot (Eng. Pat. 1370, 1859), Gossage (Eng. Pat. 2612, 1859), Wilson (Eng. Pat. 1361, 1859), Claus (Eng. Pats. 819 and 2616, 1869), Willans (Eng. Pat. 293, 1860), and Weldon (Eng. Pats. 3370 to 3390, 1876; and 444, 445, 1877). Winkler, in Chem. Ind. 1880, 129, gives a description of the method of making in a small reverberatory furnace from a mixture of salt-cake and 25–30 p.c. of coal, which was in use for many years. Essp (Zeitsch. angew. Chem. 1889, 284) also describes the production in a reverberatory furnace from salt-cake and 60 p.c. of coal-dust. In the manufacture of sodium sulphide by fusion of sodium sulphate with anthracite in a reverberatory furnace, the yield of sulphide is increased by the addition of sodium bisulphate (nitre-cake), and the product is more porous and has a darker colour. These advantages are offset by the very destructive action of the charge on the hearth of the furnace, and by the loss of sulphur as sulphur dioxide during the melting operation (P. P. Budnikoff, Chem. Zeit. 1924, 48, 278).

Gossage and Matheson (Eng. Pat. 3218, 1888) propose the mixing of a considerable quantity of NaCl with the salt-cake. Gossage and Williamson (Eng. Pat. 20921, 1892) proposed to add to the mixture of salt-cake and coal 35 or 40 parts of Leblanc black-ash waste in order to prevent the action on the furnace lining.

The Société Industriale de Pont Saint Martin and A. Piccinini (Zeitsch. angew. Chem. 1908, 782) heat the mixture in an electric furnace. Another interesting proposition is that of Gossage, Matheson and Hawlicek (Eng. Pat. 121480, 1886), who suggest the use of furnaces of the lime-kiln type.

Ellershausen (Eng. Pat. 17815, 1890) describes the difficulties in maintaining the fabric of the furnace against the action of the sulphide, and ascribes them to the overheating of the charge. He constructs his furnace with a fire-bridge 2 ft. high above the furnace-bed, and avoids overheating the bridge by cooling it by means of an internal air channel. The flue above the fire-bridge is contracted towards the centre of the furnace-bed, so that the sides do not get as hot as usual. The bed is also made to rise towards the bridge so that no melted

sulphide can accumulate there. The sides of the furnace round the bed are made of fire-bricks in such a manner that they are independent of the outer walls, and are easily renewed. Lunge thus describes the working of this furnace from his personal observation (Sulphuric Acid and Alkali, vol. iii. 296): 'The charge consists of 7 cwt. salt-cake, and $3\frac{1}{2}$ cwt. coke breeze, not specially mixed, but put in the usual way, first upon the back bed and brought there to a dark red heat without any fusion. The fusion takes place on the front bed, where the mass turns first thin, and then again thickens, just like an ordinary black-ash charge (see p. 163, col. 2, to p. 169, *Leblanc Black-ash Furnaces*), but without exhibiting the well-known "candles." It is, however, not so pasty as black-ash, and more porous. It is drawn out into an iron box after first lowering the furnace damper to prevent the product burning during the discharging. The mass cools down in these boxes without any special precautions. Sixteen such charges are finished during 24 hours with a consumption of $1\frac{1}{4}$ tons of coal. The heat is not so high as in black-ash furnaces, and the furnaces do not require much repair. . . . It is very remarkable that in this case the furnace bottoms did not suffer very much, seeing that they were made exactly like those of black-ash furnaces except that they were a little sloping from the firebridge; the slope towards the working door is common to both. The reason is probably this, that with the large quantity of small coke 50 p.c. the mass always remains porous; the infusibility of coke is also an advantage in comparison with ordinary mixing coal. During work the damper must always be kept down as much as possible to avoid unnecessary entrance of air; if this is not done the mass turns more liquid, evidently by the formation of polysulphides, and the furnace suffers much more. The crude sulphide on analysis shows only a trace of polysulphides, no sulphate at all, about $1\frac{1}{2}$ p.c. thiosulphate, and about 10 p.c. of the soda as carbonate, the remaining soda being present as Na_2S ; there is about 25 p.c. insoluble. This is certainly an excellent product.'

The crude sulphide, or sulphide 'black-ash,' was, after cooling, originally broken up into lumps, packed and sold. One or two cases, however, of fire on board ship occurred which were attributed to spontaneous combustion of the crude sulphide, and carriage in this form was stopped (J. Soc. Chem. Ind. 1896, 838). Rengade and Costeanu (Comp. rend. 1913, 156, 791) have prepared the sulphides of sodium, potassium, rubidium, and caesium in a pure anhydrous form by the direct action of sulphur vapour on an excess of the alkali metal at a temperature between 200° and 300° . On distilling off the excess of the metal, the sulphide crystallises out. They are all white, microcrystalline powders at the ordinary temperature, turning yellow as the temperature rises. The sulphides are less coloured and less soluble in their metals than the corresponding oxides, but the solubility increases with rise in atomic weight of the metal. They are more stable than the oxides, being unaltered by light, and are not decomposed by heat except at very high temperatures, when they give persulphides

and vapours of the metals (Chem. Soc. Abstr. 1913, ii. 405). The action of sodium sulphide on ferric oxide, *see* Witt (J. Amer. Chem. Soc. 1921, 43, 734; Chem. Soc. Abstr. 1921, ii. 403). The use of sodium sulphide in qualitative analyses, *see* Vortman (Chem. Soc. Abstr. 1922, ii. 653). The conversion of sodium hydrosulphide into sodium monosulphide, *see* Thomas and Rule (Chem. Soc. Trans. 1913, 871). The double colloidal sulphide of iron and sodium, *see* Horsch (Bull. Soc. chim. 1920, [iv.] 27, 777; Chem. Soc. Abstr. 1920, ii. 762).

Sodium sulphide hydrate $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$.—The crude sulphide is now all lixiviated in vats similar to those described under the Leblanc process for lixiviating Leblanc 'black-ash' (*see* Figs. 6 and 7, p. 168), the only difference being that it is necessary to keep the vats in the case of sulphide much hotter than in the case of Leblanc soda. The vat liquor, after settling, is run into crystallising cones and allowed to cool, when colourless crystals of $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ separate out, and after well draining are packed in casks. The approximate composition of the commercial product is

$\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$	Na_2S	$\text{Na}_2\text{S}_2\text{O}_3$	Na_2SO_3	
96.6	0.6	1.4	1.4	=100

The sp.gr. of the crystals is 2.471. The aqueous solution of the salt reacts strongly alkaline.

Sodium sulphide lower hydrates.—A more concentrated form of sodium sulphide is made by concentrating the vat liquor usually in caustic pots (Fig. 45, p. 218). The liquor is concentrated until the temperature rises to about 160° , when a sample will be found to test 60 p.c. Na_2S . The fire is then drawn and the pot allowed to settle for 4–6 hours, and then the sulphide is packed in an exactly similar way to caustic soda into the ordinary caustic soda drum (*see* Fig. 46, p. 219). The sulphide so prepared has the following composition:—

Na_2S	62.8	p.c.
$\text{Na}_2\text{S}_2\text{O}_3$	2.9	"
Na_2SO_4	1.1	"
NaCl	1.7	"
Fe_2O_3	0.44	"
Water (by diff.)	31.06	"
					100.0	"

The concentrated sulphide is also put on the market in disks 2–4 ins. thick and in broken pieces of various sizes. This preparation has been found by experience to be entirely free from all danger of spontaneous combustion. The constitution of this preparation is in doubt, as its composition corresponds to that of the dihydrate, but the only lower hydrates described contain $6\text{H}_2\text{O}$, $5.5\text{H}_2\text{O}$, $5\text{H}_2\text{O}$, and $4.5\text{H}_2\text{O}$ (*see* Sabatier, Chem. Soc. Abs. 1881, p. 492; Götting, *ibid.* 1886, p. 980; Parravano and Fornaini, *ibid.* 1907, ii. p. 951).

Applications.—Sodium sulphide is largely used as a depilatory in the tanning industry, and in the organic colour industry as one of the raw materials of the 'sulphur colours,' and as a solvent of these colours in the dye-bath. It is also used in the manufacture of water-glass. For the estimation of sodium sulphide in sulphide dye-baths, *see* Swann (J. Soc. Dyers, 1917, 33, 146–148; Chem. Soc. Abstr. 1917, ii. 385).

Sodium disulphide Na_2S_2 is a bright yellow micro-crystalline powder, readily soluble in water, forming a deep yellow solution. It is only sparingly soluble in cold alcohol, but with hot alcohol forms an intense green solution, which becomes yellow and turbid on further heating. The disulphide fuses to a dark red liquid.

Sodium tetrasulphide Na_2S_4 is a dark yellow crystalline powder with an olive green tinge, which becomes orange-red at 115° – 120° and melts to a dark red liquid at about 267° . It is extremely hygroscopic and readily dissolves in water forming a deep orange solution which becomes dark red on heating and slowly deposits sulphur on exposure to air (Rule and Thomas, Chem. Soc. Trans. 1914, 105, p. 177).

Sodium polysulphides (other than above) and hydrosulphides.—A trisulphide and pentasulphide of sodium have also been prepared. *See* Böttger (Annalen, 1884, 223, 335, 338), Locke and Anstell (Amer. Chem. J. 1898, 20, 592), and Hugot (Compt. rend. 1899, 129, 388), Bloxam (Chem. Soc. Trans. 1900, 77, p. 753), Küster and Heberlein (Zeitsch. anorg. Chem. 1905, 43, 53; 44, 431), Biltz and Dörfurt (*ibid.* 1906, 48, 297; 50, 67), Rule and Thomas (Chem. Soc. Trans. 1914, 105, p. 177; *ibid.* 1913, p. 380; Chem. Soc. Abstr. 1916, ii. 43; Chem. Soc. Trans. 1917, 1063).

When sulphur is boiled for a short time with 4 p.c. sodium hydroxide solution in an atmosphere of hydrogen the polysulphides formed contain slightly more sulphur than the trisulphide. Long boiling with excess of hydroxide reduces these to disulphides; this reduction is less rapid for more dilute hydroxide solutions. Continued boiling with excess of caustic soda reduces the disulphides very slowly and very incompletely to monosulphides.

Thiosulphates are also formed and the ratio of the monosulphide sulphur to the thiosulphate sulphur is always slightly below unity (Tartar and Draves, J. Amer. Chem. Soc. 1924, 46, 574).

Analytical.—Treadwell's method, titrating the acidified solution of the salt with iodine, is the most satisfactory volumetric method for determining the sodium sulphide content of preparations of the salt. *See also* Berl and Pfannmüller (Chem. Zeit. 1924, 48, 115). The iodometric method of determining sodium sulphide in solution suffers from the disadvantage that sulphites and thiosulphates, which may be present in commercial sodium sulphide, will also decolorise the iodine solution.

These salts do not affect the determination of sodium sulphide if the latter is carried out by allowing the solution to run into a standard ammoniacal zinc solution until a drop of the latter just stains lead acetate paper. Alternatively, the standard zinc solution may be run into a known volume of sodium sulphide solution until the latter just fails to stain the test-paper. Somewhat more accurate results are obtained by allowing a known volume of the sulphide solution to flow into excess of alkaline copper sulphate solution, separating and washing the copper sulphide, dissolving it in nitric acid and depositing the copper electrolytically. One mg. Cu = 1.227 mg. Na_2S . The copper solution is prepared in a similar way to Fehling's solution and should contain about 50 grms. of copper

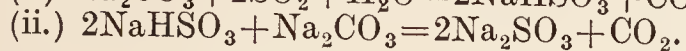
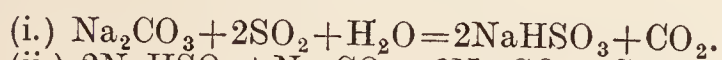
sulphate crystals per litre (V. Hassreidter, Chem. Zeit. 1923, 47, 891; J. Chem. Soc. Abstr. 1924, 126, ii. 123; E. Berl and W. Pfannmüller, Chem. Zeit. 1924, 48, 115; J. Soc. Chem. Ind. 1924, 43, B. 292).

A satisfactory method consists in titration with iodine solution after treatment with carbon dioxide until the whole of the sodium sulphide is converted into hydrogen sulphide, and the free alkali, together with that formed from the sodium sulphide, is converted into sodium bicarbonate. Thiosulphate is not attacked thereby, and can also be determined iodimetrically (E. Crespi, Atti I. Congr. naz. Chem. pur. appl. 1923, 488; Chem. Zentr. 1924, 95, i. 1977; J. Soc. Chem. Ind. 1924, 43, B. 465). For the action of sodium sulphide on iodine and the use of reaction in analyses, see Ehrlich (Zeitsch. anorg. Chem. 1918, 57, 21; Chem. Soc. Abstr. 1918, ii. 125).

For the determination of the monosulphide equivalent of the polysulphides in presence of free hydroxide and thiosulphate the following method has been devised: To 50 c.c. of a borax boric acid buffer, containing 8 grms. borax and 5.5 grms. boric acid in 100 c.c. of water, 0.1 N-iodine solution is added in slight excess above the monosulphide sulphur of the solution. The latter is then added with constant stirring, and the addition of iodine continued until the thiosulphates have also reacted and iodine is just in excess; by a separate determination of the thiosulphate after removal of sulphides by a zinc solution, and the amount deducted from the first test gives the monosulphide sulphur (H. V. Tartar and C. Z. Draves, Chem. Soc. Abstr. 1924, 126, ii. 330).

Sodium sulphites, normal Na_2SO_3 , **bisulphite** NaHSO_3 , and **metabisulphite** $\text{Na}_2\text{S}_2\text{O}_5$.

Sodium sulphite, normal Na_2SO_3 . On the large scale sodium sulphite is prepared by passing sulphur dioxide through a solution of sodium carbonate or through a vessel filled with crystals of $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$, until the product has an acid reaction. Should the strength rise above 35°Bé. , the bisulphite NaHSO_3 will crystallise out, and to prevent this some steam is blown in. The resulting solution of 35°Bé. , consisting chiefly of bisulphite, is converted into the normal sulphite by adding sodium carbonate to the boiling solution until no more carbon dioxide is evolved.



The liquid is then evaporated to 40°Bé. , settled, decanted, and set to cool and crystallise. The crystals are $\text{Na}_2\text{SO}_3 \cdot 7\text{H}_2\text{O}$. The process is conducted in wooden vessels lead lined. The vessels may also be arranged in series so as to ensure the complete absorption of the sulphur dioxide (Chem. Ind. 1899, 337). The manufacture of sodium sulphite is described in Holblings Die Fabrikation der Bleichmaterialien, 1902, p. 266.

Other methods have been proposed; thus the anhydrous salt can be obtained by heating a mixture of the requisite amounts of sodium bisulphite with sodium bicarbonate in an atmosphere of carbonic acid (Chem. Ind. 1895, 251, also Chem. Tech. der Neuzeit Dammer, 1910, 1, 135-138), and again by treating a

solution of ammonium sulphite with sodium chloride and ammonia gas (Dresel and Lemshoff, D. R. P. 80185).

The solution of sodium sulphite, if crystallised above 22° , forms the anhydrous salt Na_2SO_3 in hexagonal crystals with a sp.gr. of 2.633 at $15^\circ/4^\circ$, whereas, if crystallised below 22° it forms the heptahydrate $\text{Na}_2\text{SO}_3 \cdot 7\text{H}_2\text{O}$ in monoclinic crystals with a sp.gr. of 1.594 at $15^\circ/4^\circ$ (Hartley and Barrett, J. Chem. Soc. 1909, T. 1178) the crystals effloresce in the air.

The solubility has been determined by Kremers and by Mitscherlich (Pogg. Ann. 1827, 12, 140) and more recently by Hartley and Barrett, who found the solubility above 22° to be almost constant at 28.2 grms. Na_2SO_3 , while the metastable solubilities of the heptahydrate, and the supersolubilities of the same, are very much higher. Below the transition point the solubility of the heptahydrate is at

-1.9°	$+2.0^\circ$	5.9°	10.6°	18.2°
13.09	14.82	17.61	20.01	25.31

The solutions of sodium sulphite oxidise rapidly in the air, but Lumière and Seyewetz (Revue gén. chim. pur. et app. 1896, 7, 111) state that solutions of 20 p.c. are stable, and potassium thiocyanate and mannitol retard the oxidation, while small quantities of copper sulphate greatly accelerate it. For the atmospheric oxidation of sodium sulphite, see Dhar, Datta and Bhattachargga (Proc. K. Akad. Wetensch. Amsterdam, 1920, 23, 299; Chem. Soc. Abstr. 1921, ii. 36). For the oxidation and preservation of solutions of quinol and sodium sulphite, see Pinnow (Zeitsch. Elektrochem. 1913, 19, 262; Chem. Soc. Abstr. 1913, ii. 398; see also Chem. Soc. Abstr. 1913, ii. 1001). The alkylation of sodium sulphite, see Baggesgaard-Rasmussen and Werner (Bull. Soc. chim. 1921, [iv.] 29, 1073; Chem. Soc. Abstr. 1922, i. 104). For the absorption of nitric oxide by solutions of ferrous sulphate and sodium sulphite, see Moser and Herzner (Zeitsch. anal. Chem. 1924, 64, 81; Chem. Soc. Abstr. 1924, 126, ii. 545).

The solution is employed as a gentle bleaching agent for wool and silk; as an antichlor after bleaching yarns, cloths, or paper pulp with chlorine; as a preservative for foodstuffs; and for addition to raw sugar solutions before evaporation to prevent them colouring. It also finds application in medicine as an antiseptic and as an antizymotic for internal use. Its solution has been proposed for use in gas analysis, owing to its power of absorbing nitric oxide. It is extensively employed in the preparation of photographic developers for preventing the oxidation of the pyrogallol, hydroquinone, &c., which these contain, and has been proposed by Abney (Phot. News, 1885, 370) as a substitute for the sodium thiosulphate used to dissolve out the unaltered silver salts in the process of fixing photographic prints. For the photochemical oxidation of solutions of sodium sulphite, see Mathews and Weeks (J. Amer. Chem. Soc. 1917, 39, 635; Chem. Soc. Abstr. 1916, ii. 230).

A large number of double sulphites of sodium with other metals are known, the most interesting being the sodium potassium sulphite, which was formerly thought to exist in two isomeric forms. This view has, however, been shown to be incorrect (Barth, Zeitsch. physikal. Chem.

1892, 9, 176; Arbusoff, J. Russ. Phys. Chem. Soc. 1909, 41, 447).

For an examination of the binary system sodium sulphite—water by extrapolation from the ternary system sulphite—sulphate—water, see N. B. Lewis and A. C. D. Rivett (Chem. Soc. Trans. 1924, 125, 1156).

For the miscibility of anhydrous sulphite and sulphate of sodium, see N. B. Lewis and A. C. D. Rivett (Chem. Soc. Trans. 1924, 125, 1162).

For the action of heat in a vacuum on sodium thiosulphate and sulphite, see Picon (Compt. rend. 1924, 178, 1548; Chem. Soc. Abstr. 1924, ii. 479).

Sodium bisulphite NaHSO_3 is produced by saturating a solution of sodium carbonate with sulphur dioxide. The preparation is described in Hölbling's *Die Fabrikation der Bleichmaterialien*, 1902, 269. It forms a white powder, smelling of sulphur dioxide, is only sparingly soluble in water, and is precipitated from its aqueous solution by alcohol. On heating, it decomposes, evolving sulphur and sulphur dioxide and leaving a residue of sulphate. A crystallised trihydrate and tetrahydrate have been obtained by strongly cooling the solution of the bisulphite made in the above-mentioned way; both are very unstable, and rapidly change into the stable metabisulphite (see below).

The boiling solution has the property of readily dissolving the resin, gum, &c., contained in wood without in any way affecting the cellulose, and is used in preparing the 'sulphite pulp' now so largely made from wood for use in the manufacture of paper. It is also employed in the calico-printing and colour industries as a reducing agent, and as a specially energetic 'antichlor' for removing the last traces of chlorine from the bleached pulp obtained in paper-making. It also finds application as an antiseptic for steeping grain, preserving food, &c., and a strong solution is employed as a sterilising medium for brewers' casks (see vol. ii. 54). Owing to its property of combining with many organic aldehydes and ketones to form crystalline, mostly insoluble, additive compounds which can easily be isolated and purified, it is used in the laboratory in the identification and purification of these classes of compounds.

Sodium hydrogen sulphite. According to Schüler and Wilhelm (Zeitsch. angew. Chem. 1919, 32, 198) the sodium hydrogen sulphite crystals deposited at low temperatures from aqueous solutions contain three molecules of water. They are 2–6 cm. long, 2–3 mm. thick, hexagonal in section, and belong apparently to the rhombic system. At higher temperatures or when removed from the mother-liquor, they rapidly lose water and disintegrate, leaving a residue of anhydrous sodium hydrogen sulphite containing sulphate and traces of pyrosulphite if they had been exposed to the air (Chem. Soc. Abstr. 1919, ii. 341).

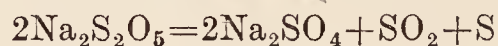
For the action of sodium hydrogen sulphite on nitro-compounds, see Weil and Moser (Ber. 1922, 55 [B], 732; Chem. Soc. Abstr. 1922, i. 443).

Sodium iridosulphite. See Sailer (Zeitsch. anorg. Chem. 1921, 116, 209; Chem. Soc. Abstr. 1921, ii. 513).

Sodium metabisulphite $\text{Na}_2\text{S}_2\text{O}_5$ is prepared by the continued treatment of a solution of sodium carbonate with sulphur dioxide, when the solution is cooled it is obtained in anhydrous crystals.

It is also made technically by passing sulphur dioxide over monohydrated sodium carbonate (Carey and Hurter, Eng. Pat. 4512, 1882).

The salt only slowly oxidises on exposure to air at the ordinary temperature; on cautious heating at 80° it loses 1 molecule of SO_2 , and on further rapid heating evolves sulphur and sulphur dioxide, leaving sodium sulphate

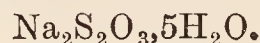


(Schultz-Sellack, J. pr. Chem. [i.] 110, 459).

It is extensively used in the preparation of photographic developers (like sodium sulphite, which see, p. 259, col. 2).

Sodium thioantimonate. According to Langhans (Zeitsch. anal. Chem. 1921, 60, 91) sodium thioantimonate solution yields the following reactions with various metallic salt solutions:—Aluminium, chromium, manganese, orange-red precipitates; zinc, cadmium, yellow precipitates; iron, nickel, cobalt, bismuth, black precipitates; silver, copper, lead, reddish-brown precipitates. With mercury salts, the coloration of the precipitate varies with the salt: mercuric oxalate, mercuric oxide, and mercurous nitrate are blackened, whilst mercuric bromide gives a yellow precipitate. Mercuric cyanide yields a yellow precipitate which changes to black, and mercuric chloride gives a red precipitate which gradually changes to white. Mercury fulminate is at first coloured yellow, but this colour soon changes to green and finally to black. Mercury potassium iodide yields an orange-coloured, flocculent precipitate (Chem. Soc. Abstr. 1921, ii. 353).

Sodium thiosulphate (formerly **hyposulphite** and still frequently so called)



This compound was first prepared in 1799 by Chaussier.

Small quantities of the salt may be made by taking about 1 lb. of pure, well-dried sodium carbonate, mixing with it about one-third its weight of flowers of sulphur, and then heating the mixture in a porcelain basin to the melting-point of sulphur for some time, stirring well all the while, so as to bring every part in contact with the air. Oxygen is absorbed by the sodium sulphide formed, which is converted, with feeble incandescence, into sodium thiosulphate. When cold, the mass is dissolved in water, boiled with sulphur for some time, and the liquid concentrated by evaporation to the crystallising-point. A very pure product may be thus obtained.

It can be prepared by boiling a solution of sodium sulphite with flowers of sulphur, filtering from the excess of the latter, and allowing the solution to crystallise $\text{Na}_2\text{SO}_3 + \text{S} = \text{Na}_2\text{S}_2\text{O}_3$. Hargreaves and Dunningham (J. Soc. Chem. Ind. 42, Trans. 147–152) have studied the method because the processes of Loch, Schaffner, Schutz, and Kopp were dependent for their calcium sulphide on the Leblanc soda process (p. 160, col. 2, method 8, and especially p. 169, col. 1,

last par. and col. 2, first par.). The reaction is initially a rapid one, but as it proceeds the very soluble thiosulphate formed rapidly reduces the solubility of the sodium sulphite—

Percentage of the solution—

$\text{Na}_2\text{S}_2\text{O}_3$.	0	10	20	30	40	50
Na_2SO_3 .	22	13	7	3	2	1.3

This causes the reaction to become gradually slower, but by increasing the amount of the slightly soluble ingredients the reaction becomes sufficiently rapid. The plant used commercially consisted of a steam-heated digester with agitator, a vacuum filter also steam-heated, a mechanical crystalliser, and a centrifugal machine. The crystals do not require purification as the impurities are left with the excess of the ingredients on the filter bed, and these residues are re-used in following batches until the impurities become too great.

Another method consists in boiling sulphur with soda-lye and passing sulphur dioxide into the yellow solution until it becomes colourless.

The anhydrous salt is easily prepared by passing air over anhydrous NaSH at a temperature of 100° – 150° .

Losh's process is as follows: The tank waste produced in Leblanc alkali works, consisting essentially of calcium sulphide (see references just above), is exposed to the air for a week or more, being turned over from time to time, so as to bring every portion in contact with air, oxygen is absorbed, heat evolved, and calcium thiosulphate is formed and a little sodium thiosulphate. The mass is then lixiviated with water, and to the clarified liquor sodium carbonate solution is added in sufficient quantity to convert all lime salts into calcium carbonate. The clarified solution is drawn off, concentrated by evaporation, and the crystals of sodium thiosulphate purified by recrystallisation. As the clarified liquor from the oxidised tank waste always contains a portion of polysulphides which discolour the final product, the liquor is run down a coke tower up which is forced a current of air and a little steam; the polysulphides are oxidised to thiosulphate and the liquor becomes acid. The exit solution is neutralised with milk of lime, evaporated to a sp.gr. of 1.25, and a solution of sodium sulphate added until the precipitation of the calcium is complete. The precipitate, consisting chiefly of calcium sulphate, but containing also from 2 to 5 p.c. sodium and calcium sulphites and thiosulphates, is dried at 100° , and sold to the paper-makers, the calcium sulphate serving as a weighting material and the contained sulphites, &c., act as antichlor. The filtered solution is evaporated to a sp.gr. of 1.65 and allowed to cool, when sodium thiosulphate and a little sulphite crystallise out.

Schaffner (Dingl. poly. J. 193, 42) treats the yellow liquid extract of the oxidised tank waste with sulphur dioxide, exactly neutralises the excess of the latter by the addition of a further quantity of fresh sulphide liquor, heats to 75° – 90° , and adds the requisite amount of sodium sulphate (determined by the analysis of a sample of the liquid), and finally, a little caustic soda is added to ensure the complete precipita-

tion of the calcium sulphate. If traces of sulphides are still present they are removed by the addition of a little sodium bisulphite, and the clear solution is then evaporated to 43° Beaumé and allowed to crystallise. The crystals so obtained are sold directly for use as an antichlor, but if required for photographic purposes they are recrystallised once in stoneware pans.

Schutz's method (J. Soc. Chem. Ind. 30, 618) is to mix tank waste with the requisite amount of sodium sulphate, and to render the mass more porous and moist by adding also the insoluble residue from previous operations. The mixture is formed into great heaps; the temperature rises to 80° in the interior, and in 4–6 days the operation is complete, and the mass contains then 26 p.c. sodium thiosulphate. It is transferred to a series of lixiviating tanks like black-ash lixiviation tanks (see under *Sodium carbonate*, Leblanc process, p. 167, col. 2, last two pars.) and lixiviated; the solution is purified from polysulphides by sulphur dioxide, evaporated and crystallised.

Kopp's method is to mix the tank waste with 10–15 p.c. of sulphur and 12–15 times its weight of water and boil for 1 hour. The insoluble calcium sulphide is thus converted into soluble calcium polysulphide. The solution is put into a closed vessel, where it is agitated with sulphur dioxide which converts the calcium polysulphide into calcium thiosulphate, which by addition of sodium sulphate is converted into sodium thiosulphate solution and calcium sulphate, which last being filtered off the clear liquor is evaporated and crystallised.

In Moody's patented process, strontium sulphide—obtained by reducing strontium sulphate by means of powdered coal—while still hot, is mixed with water to form a thin paste. The mass is boiled with sufficient caustic alkali to combine with the sulphur of the sulphide. Strontium hydroxide crystallises out on cooling, and the mother-liquor consists of solution of sodium sulphide. On treating this liquor with sulphur dioxide, sodium thiosulphate is formed, and free sulphur deposited (J. Soc. Chem. Ind. 3, 30).

Another process consists in the reduction of sodium sulphate by furnacing with coal, extraction of the Na_2S so obtained by water, and the treatment of this sulphide solution with sulphur dioxide.

Sodium thiosulphate may also be prepared from the spent lime of the purifiers of gas works, which contains the calcium salt of thiosulphuric acid as well as calcium sulphide.

Other patents for the technical manufacture of sodium thiosulphate are: Verein Chemischer Fabriken zu Mannheim, Eng. Pat. 23217 *b* and *c*, 1907 (air is passed over anhydrous NaHS at 100° – 150°), and the anhydrous sodium thiosulphate produced is either marketed in that form, or else is dissolved out and crystallised and converted into the hydrate with $5\text{H}_2\text{O}$; Sidler, D. R. PP. 81437 and 84240 (sodium sulphite is heated with fused sulphur in CO_2); Verein Ch. Fab. zu Mannheim, D. R. P. 38594 (production of sodium thiosulphate by the action of SO_2 and steam on a mixture of NaHSO_3 and S in presence of water); Clemm, D. R. PP. 180554 and 185030. A mixture of about 430 parts of Na_2SO_4 , 180 parts bauxite,

and 70 parts coal is heated and yields sodium aluminate and sodium polysulphide; the mass is lixiviated and the yellow-green clear solution is treated with SO_2 to obtain a precipitate of pure alumina, and a solution of $\text{Na}_2\text{S}_2\text{O}_3$.

Properties.— $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ forms large transparent prisms, belonging to the monoclinic system. Its solution is neutral to litmus paper; it is without smell, has a cooling taste, and does not change on exposure to air. The crystals melt in their water of crystallisation at 48.2° . The salt has a sp.gr. of 1.672. It dissolves very readily in water with considerable absorption of heat. The weakest saturated solution is obtained at -10° with 30 p.c. $\text{Na}_2\text{S}_2\text{O}_3$; on increasing the temperature to 48° the saturated solution contains 63 p.c. $\text{Na}_2\text{S}_2\text{O}_3$, and between these temperatures the crystalline solid is $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$. From 48° to 68.5° the solution increases in strength to 69 p.c. $\text{Na}_2\text{S}_2\text{O}_3$, and the crystalline solid is $\text{Na}_2\text{S}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$. Above 68.5° the strength increases but slowly, and the crystalline solid is anhydrous $\text{Na}_2\text{S}_2\text{O}_3$ (J. Soc. Chem. Ind. 42, Tran. 148, Hargreaves and Dunningham). It easily forms supersaturated solutions, which may be made to contain as much as 217 parts of the salt in 100 of water at 0° . It is insoluble in alcohol.

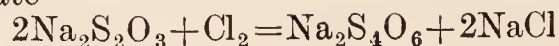
The action of acids and formaldehyde, *see* Vanino and Schinner (Ber. 1914, 47, 2562; Chem. Soc. Abstr. 1915, i. 371). The action of chlorine, *see* Self (Pharm. J. 1915, 95, 133; Chem. Soc. Abstr. 1915, ii. 683). Action on hypochlorites, *see* Dienert and Wandenbulcke (Compt. rend. 1919, 169, 29; Chem. Soc. Abstr. 1919, ii. 336).

The reaction between halogen cyanides, *see* Kurtenacker; Kurtenacker and Fritsch (Chem. Soc. Abstr. 1921, ii. 502). Detoxication of inhaled hydrocyanic acid, *see* Teichmann and Nagel (Biochem. Zeitsch. 1919, 93, 312; Chem. Soc. Abstr. 1919, i. 301). The kinetics of the reaction between hydrogen peroxide and sodium thiosulphate, *see* Abel (Chem. Soc. Abstr. 1913, ii. 766; Abel and Baum, *ibid.* 1913, ii. 399). Decomposition of mercury fulminate, *see* F. H. and P. V. Dupré (Analyst, 1921, 46, 42; Chem. Soc. Abstr. 1921, i. 232). *See also* Mercuric fulminate, vol. iv. p. 280. *See* Rudolf Hac (Eighth Inter. Cong. App. Chem. 1912, i. 205; Chem. Soc. Abstr. 1913, ii. 730) for the quantitative precipitation of metallic compounds. For the cryoscopy of sodium thiosulphate, *see* Boutaric and Leenhardt (Bull. Soc. chim. 1913, [iv.] 13, 361; Chem. Soc. Abstr. 1913, ii. 669).

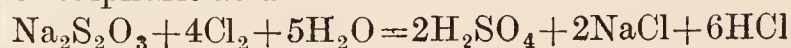
Other forms.—A large number of hydrates other than with $5\text{H}_2\text{O}$ have been prepared and their solubilities at various temperatures studied by Young, Mitchell, and Burke (J. Amer. Chem. Soc. 1904, 26, 1389 and 1413; 1906, 28, 315). The anhydrous salt with sp.gr. 1.667, is prepared as already described by the Chem. Fabrik Mannheim, and also by carefully drying the usual hydrate.

Applications of Sodium Thiosulphates.—They are used as an antichlor for removing the last traces of the chlorine from bleached fabrics. The course of the reaction is governed by the strength of the solutions, the temperature, the neutrality and the manner of

mixing; the product may be sodium tetrathionate



or sulphuric acid



and some sulphides are formed, by still other reactions (Bolley's Technologie Neue Folge. 1909, 16, 74).

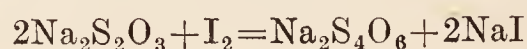
They find extended application in photography. A solution is employed to dissolve out the unaltered silver halogen compound from the negatives or prints which are thus 'fixed' and rendered unalterable on exposure to light. It is also used as a source of sulphur dioxide in the bleaching of wool, straw, oils, ivory, bones, &c. As a preservative against fermentation it is used in the sugar industry. In the calico-printing and dyeing trades it is employed in the preparation of mordants, thus aluminium sulphate is treated with sodium thiosulphate, and the resulting solution of aluminium thiosulphate thickened as usual and printed on the fibre; on steaming the printed cloth, alumina is deposited on the fibre by the decomposition of the aluminium thiosulphate, and the material can then be dyed with alizarin, &c. They have been used to fix aniline greens; and in conjunction with salts of copper to produce the so-called 'argentine effects' which depend upon the deposition of a thin film of copper sulphide on the fibre. Sodium thiosulphates are also employed in the preparation of various artificial colours; in the reduction of indigo; in the wet methods of preparation of antimony cinnabar, and ordinary cinnabar; in metallurgy for wet silver-extraction processes, the silver being converted into chloride by roasting the ore with common salt, and the mass lixiviated with a solution of the sodium thiosulphate (*v.* SILVER); in the preparation of silvering and gilding solutions, and in the extraction of gold from ores.

The property which the salt possesses of fusing at a low temperature in its water of crystallisation and solidifying again on cooling has been utilised by Fleck in sealing glass tubes containing explosives to be used under water in torpedoes.

In medicine sodium thiosulphate is used in cases of sarcinous vomiting, and as an external application in parasitic skin diseases.

For the oxidation procedure in the human organism, *see* Lasch (Biochem. Zeitsch. 1919, 97, 1), who states that 12 grms. per day of sodium thiosulphate can be consumed without harm.

In the laboratory the salt is largely used for volumetrically determining residual free iodine (iodometry) the fundamental reaction being—



For the application of this, *see* the article on ANALYSIS, vol. i. 270, and Mohr's Chem. Analyt. Titrimethoden, p. 282. It is suggested that the alteration of standard volumetric solutions of sodium thiosulphate on keeping may be due to their decomposition into sulphite and sulphur, which, under the influence of hydrogen ions or of carbon dioxide, combine to form the co-ordination complex $\text{Na}_2\text{S}_2\text{O}_3 \dots \text{S}$. New and old solutions in presence of excess of ZnO react differently to KMnO_4 solution (F. Feigl, Ber.

1923, 56, 2086-2088; J. Soc. Chem. Ind. 1923, 42, 1204 A). It has also been proposed for use in quantitative analysis for the precipitation of various metals in place of sulphuretted hydrogen; lead, mercury, silver, copper, and cadmium are all quantitatively precipitable as sulphides, and chromic and aluminium salts are precipitated as hydroxides, by boiling their solutions with sodium thiosulphate (Faktar, Zeitsch. anal. Chem. 1900, 39, 345). For the reduction of silver thiosulphate by hyposulphite, see Steigmann (Kolloid. Zeitsch. 1920, 27, 249; Chem. Soc. Abstr. 1921, ii. 46, 147). For the compounds of silver thiosulphate and acetylene-silver acetylide, see Bhaduri (Zeitsch. anorg. Chem. 1913, 79, 355; Chem. Soc. Abstr. 1913, i. 241).

The preparation, testing, and application of various substances for the standardisation of thiosulphate solutions are described in detail, and their relative merits for the purpose discussed by Kolthoff (Pharm. Weekblad, 1919, 56, 644). The purest forms of potassium dichromate obtainable commercially contain free chromic acid or potassium chromate. A method for the detection and estimation of these is given, which depends on the location of a discontinuity in the conductivity curve on the addition of alkali or acid. If chromic acid is present the addition of standard alkali causes no increase in the conductivity of a dichromate solution until the free acid is neutralised. Similarly, no increase in conductivity is observed on the addition of acid to a solution containing chromate until all the latter has been converted into dichromate. For analytical purposes it is recommended to melt the pure dichromate in an electric furnace before use. The other substances examined are iodine, oxalic acid, cyanogen iodide, potassium iodate, and potassium bromate. All these are easily purified, and give results in the titration of thiosulphate with an error of less than 0.1 p.c. The greatest error, 0.07 p.c., was observed in titrating with dichromate (Chem. Soc. Abstr. 1920, ii. 49). See also Bertiaux (Chem. Soc. Abstr. 1920, ii. 554). According to Low (Chem. Soc. Abstr. 1921, ii. 133) the standard solution will keep almost indefinitely if stored in amber-glass bottles and treated with about 5 grms. of sodium hydroxide per litre to neutralise any carbonic acid present. It is standardised against the ordinary permanganate solution (the iron value $\times 1.139$ = the copper value). About 35 c.c. of the permanganate solution are added to 150 c.c. of water, 5 c.c. of glacial acetic acid, and 6 c.c. of 50 p.c. potassium iodide solution, the liberated iodine is titrated with the thiosulphate solution until the colour is faint, starch and 2 c.c. of silver nitrate solution (about 4 grms. per litre) are added, and the titration is completed. The yellow colour of the silver iodide produced destroys the purple tinge of the mixture, and the delicacy of the end-point is thus enhanced. This method of standardisation is rapid and is recommended as being possibly more accurate than that based on the use of metallic copper. Hampsue and Pratt (Pharm. J. 1913, 91, 142) found that the strength of $N/2$ and $N/10$ sodium thiosulphate solutions remained stable after the solutions had been kept for eight months under varying conditions as to the exposure to light and the colour of the bottles in which they had been stored. In certain cases

small quantities of sulphur separated but the decomposition was not of such a degree as to affect the titre of the solutions (Chem. Soc. Abstr. 1913, ii. 786). See also Kolthoff (Pharm. Weekblad, 1919, 56, 878; Chem. Soc. Abstr. 1919, ii. 341); Bohrisch (Pharm. Zeit. 1914, 59, 360; Chem. Soc. Abstr. 1914, ii. 482); Waterman (Chem. Weekblad, 1918, 15, 1098; Chem. Soc. Abstr. 1918, ii. 404).

Sodium thiosulphate is employed in the separation of iron and aluminium. A solution containing these two metals is treated in the cold with sodium thiosulphate; this gives rise to the aluminium thiosulphate, and when boiled it is decomposed, with evolution of sulphur dioxide and deposition of sulphur and alumina, while the iron salt is not further acted upon than to reduce all ferric salts to ferrous salts.

Sodium thiosulphate double salts.—Sodium thiosulphate forms a large number of double salts, many of which are of extremely complex composition. Those formed with copper and silver have been studied by Rosenheim and Steinhäuser (Zeitsch. anorg. Chem. 1900, 25, 72) and C. and I. Bhaduri (*ibid.* 1898, 17, 1). See also L. Shinn (J. Amer. Chem. Soc. 1904, 26, 947). Sodium stibio-thiosulphate, see Julius von Szilágyi (Zeitsch. anorg. Chem. 1920, 113, 69; Chem. Soc. Abstr. 1921, ii. 207).

Sodium thiosulphate and cupric nitrate in cold aqueous solution produce disodium tri-cuprous thiosulphate



crystallising in yellow needles which, when well washed and air dried, are permanent. Other similar salts can also be prepared (Bassett and Durrant, Trans. Chem. Soc. 1923, 123, 1279).

Sodium thiosulphate, fused in its water of crystallisation, dissolves freshly prepared cuprous halides and cuprous thiocyanate, giving clear colourless aqueous solutions from which are obtained crystalline complex compounds unaffected by light (G. Canneri and R. Luchini, Gazz. chim. ital. 1922, 52, ii. 261). Sodium thoromolybdates, see Barbieri (Atti R. Accad. Lincei, 1913, [v.] 22, i. 781; Chem. Soc. Abstr. 1913, ii. 779).

Sodium trithiocarbonate $\text{Na}_2\text{CS}_3, \text{H}_2\text{O}$ is obtained by adding the requisite amount of carbon disulphide to an alcoholic solution of sodium hydrosulphide or disulphide and adding ether when the thiocarbonate separates out. It forms deliquescent needles of a pinkish-yellow colour, and gives a reddish solution in water which is stable out of contact with oxygen or carbon dioxide. The *perthiocarbonate* $\text{Na}_2\text{CS}_4, 3\text{H}_2\text{O}$, formed in the same way, crystallises in deliquescent brownish-yellow needles and gives a yellow aqueous solution. The heats of formation of sodium trithiocarbonate and sodium perthiocarbonate in alcoholic solution are, respectively, 5700 and 8550 cal. (Yeoman, Chem. Soc. Trans. 1921, 119, 38).

Sodium tungstate. For compounds of sodium with tungsten and tungsten derivatives, and the manufacture of sodium tungstate and its properties, see Art. TUNGSTEN, vol. vii. See also Smith (J. Amer. Chem. Soc. 1922, 44, 2027; Chem. Soc. Abstr. 1922, ii. 774). For the transformation points, see van Klooster and Germs (Zeitsch. anorg. Chem. 1914, 86, 369; Chem. Soc.

Abstr. 1914, ii. 460). For the equilibrium of sodium tungstate with sodium silicate and with potassium tungstate, see van Liempt (*Zeitsch. anorg. Chem.* 1922, 122, 175; *Chem. Soc. Abstr.* 1922, ii. 775). Specimens of sodium tungstate which are not alkaline to phenolphthalein contain complex tungstates. They may be suitable for use in Otto Folin's (*J. Biol. Chem.* 1922, 51, 419) system of blood analysis by addition of the requisite quantity of alkali (*Chem. Soc. Abstr.* 1922, ii. 595). For the preparation of sodium paratungstate, see Lottermoser (*Kolloid Zeitsch.* 1922, 30, 346; *Chem. Soc. Abstr.* 1922, ii. 510). For the action of sodium paratungstate in fusion on salts of the halogen acids and oxy-halogen acids, see Kuzirian (*Amer. J. Sci.* 1913, [v.] 36, 301; *Chem. Soc. Abstr.* 1913, ii. 865 and 872). The use of sodium paratungstate in the estimation of the metal in cyanides, see Kuzirian (*J. Amer. Chem. Soc.* 1917, 39, 2356; *Chem. Soc. Abstr.* 1918, ii. 82). Sodium oxalotungstite, see Collenberg (*Chem. Soc. Abstr.* 1920, ii. 115).

Sodium zincate. The solubility isotherm in the system $\text{Na}_2\text{O}-\text{ZnO}-\text{H}_2\text{O}$ has been completely determined at 30° by dissolving zinc oxide in solutions of sodium hydroxide of various concentrations and determining the solubility. The following substances appear as stable, solid phases: zinc oxide, sodium zincate, Na_2O , ZnO , $4\text{H}_2\text{O}$, and the monohydrate of sodium hydroxide. Sodium zincate forms very strongly incongruent solutions; in solutions containing 1 part of sodium hydroxide to 2 parts of water, it is decomposed, with separation of zinc oxide. Amorphous, gelatinous zinc hydroxide is to be regarded as a phase of a varying water content; it is impossible to remove all adsorbed ions from it, and it is metastable as regards zinc hydroxide. In special circumstances zinc hydroxide may be obtained as a crystalline phase of the constant composition, $\text{Zn}(\text{OH})_2$. This crystallised hydroxide is metastable at 30° with respect of zinc oxide (Goudriaan, *Proc. K. Akad. Wetensch. Amsterdam*, 1919, 22, 179; *Chem. Soc. Abstr.* 1920, ii. 113). See ZINC OXIDE, vol. vii.

H. B.

SOFT CEMENTS *v.* LUTES.

SOILS. (1) *Classification.*—Various classifications of soils have been proposed, the most general may be described as 'Genetic,' in which the position of the soil is determined by its origin, and the factors of climate and vegetation which have given rise to it. Tulaikoff (*J. Agric. Sci.* 1908, 3, 80) distinguishes:

1. Laterite soils developed in humid tropical climates and marked by a large proportion of hydrated ferric oxide and alumina.
2. Wind-blown loess soils.
3. Soils of the dry steppes, distinguished by their richness in soluble salts, often alkaline.
4. Black soils (Tchernozem), containing large quantities of neutral humus.
5. Gray forest soils, containing less humus, to which group most of the soils of Great Britain belong.
6. Peat and ashy soils (Podzol).
7. Tundra soils.

Under British conditions we may distinguish between sedentary soils which have arisen *in situ* through the weathering of the underlying rock, and drift soils (soils of transport or alluvial soils) which have reached their present position

through the action of running water or ice. The mixed soils of steep slopes which have either been washed or rolled down from above and containing angular fragments of diverse origin are sometimes separated as colluvial soils.

The farmer is accustomed to classify soils according to the ease or otherwise with which they can be worked, as sand, loams, and clays, with suitable subdivisions, *e.g.* sandy loams. These terms possess, however, widely different meanings according to the amount of rainfall which prevails, and can only be given any scientific value by correlating them with the mechanical analysis of the soil.

(2) *Proximate composition of the soil: mechanical analysis.*—The texture of the soil and the manner in which it will behave under cultivation are determined by the relative proportions of sand, clay, calcium carbonate, and humus or organic matter which it contains. By sand is meant the coarser particles generally consisting of silica. As it is convenient to take an arbitrary limit of size, sand may be defined as consisting of particles smaller than 1 and coarser than 0.04 mm. in diameter. Such material is distinguished by the small amount of water it will contain and by its lack of coherence when dry. Clay consists of the finest particles present in the soil and is distinguished by the large amount of water that it will retain, by its plasticity and impermeability to water when wet, and by its power of shrinking and cracking when dry and swelling again on wetting. When diffused through water, the clay particles can be flocculated or coagulated by small quantities of various soluble salts (Comber, *J. Agric. Sci.* 1920, 10). The properties of clay may be regarded as due to the fact that the finer particles are either wholly colloidal or are coated with colloids on their surface. The rate of evaporation of water from a soil containing clay pursues a different course than the corresponding rate from sand, however fine (Keen, *J. Agric. Sci.* 1914, 6, 456; *Trans. Faraday Soc.* 1922, 17). Again, the absorption properties of a soil are explicable on the assumption that the clay particles are mainly colloidal. If we take 0.002 mm. as the superior limit of size for the clay particles they run down without any break to particles of ultra-microscopic size which remain indefinitely in suspension in a neutral liquid, forming a colloidal suspension. Regarded chemically clay is mainly a hydrated silicate of alumina (kaolinite), but the chemically active portions behave as if it were a zeolite, containing in addition to the alumina easily replaceable bases—potash, soda, lime and magnesia. In the clay fraction is also included a certain amount of very finely divided ferric hydrate and silica; these particles, however, do not behave as colloids. For the purposes of analysis, the clay particles are divided by their size and not by their chemical composition. It is generally convenient to distinguish the groups of particles intermediate between sand and clay as silts.

All fertile soils contain some proportion of calcium carbonate finely disseminated throughout the soil. The proportion may vary from 60 p.c. or more in purely calcareous soils down to an inappreciable amount. Soils in which

calcium carbonate and clay predominate are usually distinguished as marls.

The organic matter of soils consists in the main of the débris of previous vegetation. It is a mixture of various complex substances, some of them containing nitrogen, and from it a few distinct compounds have been isolated (see Schreiner, U.S. Bureau of Soils, Bull. 53 and 74). In fertile soils the organic matter usually possesses a neutral reaction and consists largely of calcium salts of the so-called 'humic acid.' Humic acid does not possess any distinct composition and though it may in part be identical with the humic acid that can be prepared by the decomposition of sugar, it cannot be obtained from soil in a state free from nitrogen. Humic acid is soluble in ammonia and other alkalis and may be extracted from soil, peat, &c., by first treating the material with hydrochloric acid to decompose the calcium humate, washing, and then extracting with an alkali solution from which it may be precipitated by acid (Beckley, J. Agric. Sci. 1921, 11, 66). Soils in which the organic matter predominates are always black in colour, retentive of water and possessed of a very friable texture when dry. These peaty or boggy soils may be either acid in reaction, *e.g.* peaty and moorland soils, or neutral like the soils of the Fens.

The separation of the soil into its proximate constituents is known as a mechanical analysis, and the process consists in grading the particles (*a*) according to the velocity of the stream of water by which they can be carried, or (*b*) according to the time in which they will remain suspended in a column of water of a given height. The two methods are identical in principle and may be made to give similar results, but in most laboratories it is convenient to adopt the beaker method of separation by suspension.

A. Sampling.—In Great Britain, the layer down to a depth of 9 ins. is usually considered to represent the soil. Probably a depth of 20 cms. would have been more satisfactory, since it represents more nearly the layer which is usually stirred by the plough, but so many analyses have now been made on the 9-in. basis that it is desirable to retain the convention. In certain cases of very shallow soils the soil changes suddenly at a smaller depth than 9 ins. into something which can hardly be regarded as sub-soil, as for instance, into pure chalk rock. In these cases, the sampling must be stopped at the line of division, which should be recorded. To obtain a sample two methods are commonly employed. In the first, a steel box, 6 ins. in section, is driven into the ground to a depth of 9 ins. and its contents removed. In the second case, an auger of not more than 2 ins. in diameter is employed. It is always necessary to take a number of samples on the same piece of land and mix them before analysis, and the advantage of the auger method lies in the number of samples that can be quickly obtained without unduly increasing the bulk of material to be handled. The first sampling is usually followed by a second one, taking the second 9 ins. to represent the subsoil. Small samples for examination, and even for approximate analyses, may be rapidly obtained down to a considerable depth by means of an auger such as is used by

shipwrights. For details of sampling, Hall's 'The Soil' (Murray, 1920), p. 53, may be consulted.

The samples, on reaching the laboratory, should be spread out on shallow trays to dry at a temperature not exceeding 40°. The process is much accelerated by occasionally stirring and by crumbling down the lumps of the stiffer soils with the fingers before they become quite dry. The dried soil is passed through a brass sieve with holes 3 mm. in diameter, the lumps being gently worked down in a mortar with a wooden pestle. The material passing through the sieve is approximately weighed and also the material remaining on the sieve, which is then thoroughly washed on the sieve under a stream of running water. After drying, the stones which remain on the sieve are weighed to obtain the proportion of stones in the total sample as brought from the field. The material which passes the 3 mm. sieve is regarded as the fine earth for analysis.

B. Mechanical analysis.—Two portions of 10 grms. and one of 50 grms. of the fine earth are weighed out. One 10-grm. portion is dried for 24 hours at 100°, and then heated in an open basin over an Argand at a dull red heat with occasional stirring to obtain (1) hygroscopic moisture, (2) loss on ignition. The second 10-grm. lot is placed in a basin and covered with 100 c.c. of *N/5* hydrochloric acid to dissolve out the carbonates and break up the calcium humate. The soil is rubbed up into a fine paste with a rubber pestle made by fixing a small solid rubber bung on a stout glass rod. After standing for an hour the soil is thrown upon a tared filter and washed until all acid is removed. The filter and its contents are then dried, the loss representing the hygroscopic moisture *plus* soluble salts. The soil is now washed off the filter with water containing about 1 c.c. of ammonia in 500 c.c. water on to a small sieve made with No. 100 brass wire cloth, the portion passing through being collected in a beaker 7 or 8 c.c. in diameter with a mark on the side 8.5 c.c. from the bottom. The material on the sieve is dried and weighed to represent the coarse sand and fine gravel. As the proportion of this coarse material is likely to be affected by irregular sampling when determined on 10 grms. only, it is advisable to repeat these operations on the 50-grm. sample without, however, preserving the material passing through the sieve. The residue after drying and weighing is then divided into 'fine gravel' and 'coarse sand' by means of a sieve with round holes 1 mm. in diameter. The beaker containing the portion of the 10-grm. sample which passed through the wire cloth sieve is now well stirred with the rubber pestle, filled to the 8.5 mark with ammoniacal water and put aside to stand for 24 hours. The turbid supernatant liquid is then rapidly poured off into a large jar, and the deposit at the bottom of the beaker is rubbed up with a rubber pestle and more ammoniacal water as before. The operations of filling up to the mark, standing for 24 hours, and pouring off the turbid liquid are gone through as before and repeated every day as long as any material remains in suspension for the 24-hour period. Generally, 7 to 10 decantations will be sufficient, after which the bulk of turbid liquid is evaporated down and finally brought into a tared basin,

dried and weighed. This fraction consists of clay particles less than 0.002 mm. in diameter, together with a certain amount of humus. After drying it is heated as before and re-weighed to obtain the weight of the 'clay.' The sediment from which the clay has been removed is worked up as before in the beaker, which, however, is only filled to the depth of 7.5 cms. The contents are allowed to stand for 12 minutes only, when the liquid is poured off into a large jar as before. The operations are repeated until all the sediment settles in 12½ minutes and the liquid above is left quite clear. The contents of the second jar are now evaporated to dryness and weighed as in operation 3, before and after ignition; this fraction is designated 'fine silt' and consists of particles between 0.010 and 0.002 mm. in diameter.

The sediment remaining in the beaker is worked up afresh just as in the previous operations, the mark being now placed 10 cms. from the bottom of the beaker, and the time of settlement fixed at one hundred seconds. The sediment is dried and weighed as 'fine sand' while the portion that is poured off is obtained by evaporation as in the previous operations and is designated as 'silt.' The soil has thus been divided into the following series—

Diameter in millimetres			
	Max.	Min.	
1. Stones and gravel	—	3.0	} Separated by sift- ing.
2. Fine gravel .	3.0	1.0	
3. Coarse sand .	1.0	0.2	
4. Fine sand .	0.2	0.04	} Separated by sub- sidence.
5. Silt .	0.04	0.01	
6. Fine silt .	0.01	0.002	
7. Clay .	0.002	—	

The sizes of the particles in the above groups, which is determined by the depth of the liquid and the time of settlement, are purely conventional and are those in use by agreement in the United Kingdom. A more rapid method is described by Robinson (*J. Agric. Sci.* 1922, 12, 207).

CHEMICAL ANALYSIS.

As in a mechanical analysis, certain conventions as to the sampling, nature of the solvent, and time of its action have to be adopted. The conventions followed below are general in the United Kingdom. The air-dried fine earth passing the 3-mm. sieve is taken and a portion of about 100 grms. is ground in a mill or broken in a steel mortar until it all passes through a sieve with round holes 1 mm. in diameter. Hygroscopic moisture and loss on heating are determined as before.

For modifications of soil dried in the air, see Lebediantzer (*Compt. rend.* 1924, 178, 960; *Chem. Soc. Abstr.* 1924, i. 820).

C. Nitrogen is determined in 10 to 20 grms. of the ground material by Kjeldahl's process; no correction need be made for the nitrate that is present.

D. The determination of calcium and other earthy carbonates is of great importance, especially when the amount is low. It is not sufficient to determine the calcium, which may be present in considerable amounts as silicate, humate, &c., even when the soil is acid from lack of calcium carbonate. The earthy carbonates are best determined from the carbon

dioxide evolved on treatment with acid, being calculated as though they consisted entirely of calcium carbonate. The most exact method, when the quantity involved is small, consists in liberating the carbon dioxide by treatment with dilute hydrochloric or phosphoric acid at room temperatures in a partial vacuum, free from carbon dioxide, air being afterwards drawn through the mixture in order to wash out the last traces of carbon dioxide. The carbon dioxide may be absorbed in dilute caustic soda and determined by double titration, or by baryta solution (*see* Hutchinson and MacLennan, *J. Agric. Sci.* 1914, 6, 324). The lime requirements of the soil are best determined by estimating the calcium withdrawn by the soil on shaking with a solution of calcium bicarbonate (*see* Hutchinson and MacLennan, *J. Agric. Sci.* 1914, 6; *Chem. Soc. Abstr.* 1914, ii. 784). *See also* Sanyol (*Chem. Soc. Abstr.* 1924, i. 820).

E. For the determinations of soluble constituents, 20 grms. of the powdered soil are placed in a flask of Jena glass, covered with about 70 c.c. of strong hydrochloric acid, and boiled for a short time over a naked flame to bring the acid to constant strength containing about 20.2 p.c. of pure hydrogen chloride. The flask is loosely stoppered, placed on the water-bath, and the contents allowed to digest for 48 hours. The solution is then cooled, diluted, and filtered. The washed residue is dried and weighed as the material insoluble in acids.

The solution is made up to a litre and aliquot portions are taken for the various determinations. The analytical operations are carried out in the usual manner, but special care must be taken to free the solution from silica and organic matter.

For determination of the potash and phosphoric acid, 50 c.c. of the solution is taken and evaporated to dryness, about half a gram of calcium carbonate being added during evaporation if the soil is poor in calcium. The contents of the dish are then heated over an Argand or a Bunsen burner at a black or very dull red heat, the material being constantly stirred with a small glass pestle made by flattening out the end of a glass rod. After cooling, a few c.c. of water is added and the mass is worked up with the pestle, 50–80 c.c. of water is then added and the contents of the dish are boiled for half an hour. The solution is filtered off, the residue washed and the solution taken for determination of the potash by precipitation with platinic chloride or perchloric acid in the usual way. The residue is washed back on to the dish, 50 c.c. of water and 10 c.c. of strong sulphuric acid are added and the whole boiled for half an hour. The solution is filtered and used for the determination of phosphoric acid by precipitation with ammonium molybdate, the molybdic acid precipitate being either weighed or estimated by titration. In some cases, finely divided ferric oxide comes through the filter paper in making up the solution, in which case 5 c.c. of hydrochloric acid is added and the whole evaporated nearly to dryness. This will bring the iron into solution, when it will not interfere with the determination.

Calcium, magnesium, iron, manganese, and sulphuric acid may also be determined in the hydrochloric acid extract.

The determinations just described give what is commonly called the total plant food in the soil. It will be seen that the quantities revealed are usually very great, if we consider that the layer of soil down to the depth of 9 ins. over an acre weighs from $2\frac{1}{2}$ to 3 million pounds. As a rule, hydrochloric acid will extract something in the order of 0.1 p.c. of phosphoric acid and from 0.3 to 0.5 p.c. of potash, proportions which would correspond to about 3000 pounds of phosphoric acid and 10,000 lbs. of potash per acre, whereas the average crop will remove not more than 50 lbs. of phosphoric acid and 200 lbs. per acre of potash. It is clear that the quantities thus determined throw very little light upon the need, or otherwise, for the application of particular fertilisers to the soil, since the soil is shown to contain far more than is sufficient for a maximum crop. Even the extraction with hydrochloric acid does not measure the total amount of plant food in the soil; if, for example, the soil is completely brought into solution by fusion with ammonium fluoride as much as 2 p.c. of potash may be found in clay soils, and this quantity is in a sense the only absolute measurement that can be made.

In order to obtain by analysis some practical guidance as to the requirements of the soil, attempts have been made to discriminate between the total amount of plant food in the soil and that which may be regarded as readily available to the plant, *i.e.* that which is soluble in such weak solvents as may be at work under natural conditions. In the soil *in situ* there is every reason to suppose that the solvent action is carried on by water containing carbon dioxide in solution, partly by the natural soil water, and partly by the more concentrated solution of carbon dioxide which forms in contact with the plant roots that are always excreting carbon dioxide. As the gases entangled in the soil always contain more carbon dioxide than ordinary air (up to 5 p.c. by volume), the soil water contains a corresponding amount of carbon dioxide, and so becomes a more effective solvent of phosphoric acid and potash. Attempts have been made to use water saturated with carbon dioxide as an analytical agent to determine the available mineral constituents in the soil; but although this is the solvent with the best *à priori* justification, its use has not been general and there are not sufficient data obtained by its means for comparison. For the present, therefore, it must remain as a research method hardly available for general analytical purposes. It is customary to employ a solution containing 1 p.c. of citric acid to determine the phosphoric acid and potash that may be regarded as available. Other weak acids have been proposed, but none of them bring about any absolute discrimination between two distinct classes of material, one of which can be regarded as available for the plant, the other as dormant. All acids, when of equivalent strength, begin by dissolving the same amount of, *e.g.* phosphoric acid from the soil in question. Reabsorption, however, immediately begins and the final equilibrium that is brought about, is conditioned by the soil materials and the nature of the acid used. Other available constituents which may be taken to measure the fertility of a given soil are the nitrates and the ammonium compounds and also the humus

compounds soluble in dilute alkali—the soluble humus or *matière noire*—which represents that part of the organic matter in the soil likely to be readily oxidised.

F. *Nitrates*.—The soil sample must be rapidly dried in the steam oven, since slow drying at temperatures a little above the normal would result in the formation of nitrates. After drying the soil is roughly powdered and passed through a 3-mm. sieve as before. 200 grms. of the sample are then packed on a Buchner funnel, 6 ins. in diameter, connected with a filter pump. The soil is washed with successive portions of hot water, and if care is taken to avoid plastering the wet soil it is possible to wash all the nitrates through in the first 100 c.c. or so of the water that reaches the filtering flask. The nitrates in the solution thus obtained are estimated by the standard methods. In the Rothamsted laboratory, it has been found most convenient to proceed by reducing them to ammonia by the zinc-copper couple, as devised by Thorpe (Chem. Soc. Trans. 1873, 26, 541). Strips of thin sheet zinc about 6 ins. long and $1\frac{1}{2}$ ins. broad are cleansed by immersion in dilute caustic soda, followed by very dilute sulphuric acid, and are then dipped in a dilute solution of copper sulphate until they have obtained a heavy black deposit of copper. After washing finally in ammonia-free water they are placed in a bottle with the soil extract and a crystal of oxalic acid. The bottle is kept in a warm place or an incubator at 25° for 24 hours, then the ammonia is distilled off and determined by titration or by 'Nesslerising.'

Full details of a simple procedure for accurately determining nitrates in soils by the phenoldisulphonic acid method are given by H. J. Harper (Ind. Eng. Chem. 1924, 16, 180). Perfectly clear and colourless soil extracts are obtained by using as decolorising agent copper hydroxide precipitated in the soil suspension from copper sulphate and calcium hydroxide. Experiments show that this substance removes inappreciable quantities of nitrate from the solution by adsorption, whereas animal charcoal adsorbs appreciable quantities of nitrate. The losses of nitrate which are due to the evaporation of acid filtrates, to the presence of chlorides in excess of 15 parts per million in the soil, and to the presence of carbonates in the residue to which the phenoldisulphonic acid is added, can be prevented by keeping the solution alkaline on evaporation, by removing the chlorides with silver sulphate, and by flooding the dry residue with 3 c.c. of phenoldisulphonic acid. Interfering tints that occur in making comparisons between standard solutions and those of unknown nitrate content are caused by the presence of organic colouring matter, by irregularities in the method of adding the different reagents, and by the presence of insoluble matter in the solution. They can be avoided by removing the organic matter with copper hydroxide, by treating all residues uniformly according to the procedure given, and by filtering to remove material not in solution (J. Soc. Chem. Ind. 1924, 43, B. 268).

For a comparison of various methods of determining nitrates in soil, see D. J. R. Van Wijk (Sol. Sc. 1924, 17, 163; Chem. Soc. Abstr. 1924, 126, ii. 566).

G. For determinations of the ammonium salts, 100 grms. of the soil are placed in a distillation flask with 2 grms. of magnesia and 100 c.c. of water. The tube from the flask is connected to a 100 c.c. pipette which leads into a filter flask serving as a receiver and containing 50 c.c. of standard acid. The distilling flask is placed in a water-bath kept at 30° and the filter flask is connected with a pump to maintain a partial vacuum. Distillation at this temperature proceeds for 6 hours, after which the pipette is disconnected and the acid titrated (*see* Russell, J. Agric. Sci. 1910, 3, 233).

H. *Available phosphoric acid and potash*.—200 grms. of air-dried soil are placed in a Winchester quart bottle with 20 grms. of citric acid and 2 litres of water. By the original method (*see* Dyer, Chem. Soc. Trans. 1894, 65, 115) the contents of the bottles are shaken from time to time for 7 days and then filtered; but it has been shown that identical results can be obtained in 24 hours if the bottle is placed in an end-over-end shaker and kept in continuous agitation. After filtering, two portions, each of 500 c.c., are taken for the determination of phosphoric acid and potash by the methods previously described, after evaporation and incineration to get rid of the citric acid and dissolved silica.

I. *Soluble humus*.—10 grms. of the air-dried soil are treated with dilute hydrochloric acid in order to decompose the humus as in the method for mechanical analysis. After filtering and washing away the acid the soil is washed into a flask with 500 c.c. of 4 p.c. solution of ammonia. Flask and soil are then shaken for 24 hours, allowed to stand for several hours, and filtered until 200 c.c. of filtrate are obtained. This, representing 4 grms. of the original soil, is then evaporated to dryness in a tared basin and weighed. The basin and its contents are heated to determine the ash and inorganic matter also present, the weight of which must be deducted from the weight of soluble humus previously obtained.

J. *Soil reaction*.—A determination of the acidity or alkalinity of the soil is of great importance towards estimating its fertility. The hydrogen ion concentration varies from a *p*-concentration of 10 to 3, a fertile arable soil shows about 8, soils at either extreme being sterile. Litmus and the other indicators are of little value in the determination, soil being so well buffered. For methods, *see* Fisher (J. Agric. Sci. 1921, 11, 1).

K. *Physical determinations*.—In addition to the mechanical analysis of soils, several other physical constants of soil have, from time to time, been determined: for example, the maximum and minimum water capacity, the capillarity, the apparent and real density, the hygroscopic moisture, the heat evolved on wetting (*Benetzung-wärme*), specific heat, &c. The methods by which these determinations are made may be found in standard works on soil, but at the present time little value can be attached to the results. Most of the figures obtainable, *e.g.* hygroscopic moisture, wilting coefficient, represent particular states of equilibrium not breaks in the smooth curve showing the relations of the soil to water. In many cases, the results are conditioned by the state into which the soil has been brought by the process of

sampling, and as no satisfactory method exists of testing the soil *in situ* or bringing it in an unchanged condition into the laboratory, determinations made upon the usual samples possess no value. Further, in nearly all cases it is difficult to attach any interpretation to the results, *i.e.* to correlate them with the behaviour of the soil in the field (Hardy, J. Agric. Sci. 1923, 13, 340). To two determinations, however, some practical value may be attached, *viz.* the hygroscopic moisture and the water content when the soil is in the optimum working condition and possesses a crumb structure. Hygroscopic moisture is usually determined by exposing the dried soil in a shallow tray to an atmosphere saturated with moisture at the ordinary room temperature. The dish containing the soil is placed under a bell jar over water and the interior of the bell jar is lined with filter paper which dips into the water below. It will be found almost impossible to obtain consistent results by this method because of the deposition of dew upon the dish or the soil. A better method is to place the soil in a shallow layer in a flat boat contained in a wide tube. The tube is immersed in a water-bath, maintained at a constant temperature of 25° by a thermostat, and a slow current of air is drawn over the soil, the air current being previously bubbled through a potash bulb containing water immersed in the same bath, so as to become saturated with vapour at the temperature of the experiment. Consistent and comparable results can in this way be obtained, and the hygroscopic moisture thus determined serves as a measure of the absorbing surface possessed by the soil. The water content of the soil in its optimum working condition is a conception introduced by F. K. Cameron (J. Phys. Chem. 1910, 14, 320) and represents that condition in which the soil can be cultivated and made to break down into small particles without puddling. Several pounds of the soil in a dried condition are placed in a large basin and slowly wetted with a fine spray of distilled water; the soil is carefully worked about with the hands to equalise the wetting, and it will be found that a point is eventually reached when the soil is distinctly moist and yet can be broken down to a crumb without getting into a pasty condition. If the moisture is increased beyond this point, the soil becomes obviously wet and gets sticky and puddled when any attempt to work it is made. The experimenter must use his judgment as to when the right point has been reached, then a sample of the soil is taken and its water content determined. With a little practice it will be found that successive results can be obtained with the same soil that agree within 1 or 2 p.c. The mean of several determinations may be taken as the optimum water content.

For further particulars, the following books may be consulted: Hall, *The Soil*, London, 1920; Hilgard, *Soils*, New York, 1906; Wiley, *Principles and Practice of Agricultural Analysis*, vol. i.; Ramann, *Bodenkunde*, Berlin, 1911.

BACTERIA OF THE SOIL.

A recognition of the importance of the biological factors at work in the soil is comparatively recent, indeed it can hardly be said

to date further back than 1877, when Schloesing and Müntz showed that the formation of nitrates from the organic nitrogen compounds in the soil is a process brought about by a living agency. It is now agreed that as regards all the compounds of carbon and nitrogen present in the soil, their transformation into compounds capable of serving as food for plants is brought about by micro-organisms of one class and another, and that the fertility of the soil is very largely determined by the relative activity of the different groups. It is possible to show by the ordinary methods of plate culture that the soil contains bacteria in numbers of the order of 0·5 to 50 millions per gram of soil, and there are several important groups of bacteria which do not grow on the usual gelatine media and therefore do not get included in this account. In addition to the bacteria, the soil possesses a micro-flora of yeasts, moulds, and other fungi, while latterly certain higher organisms—protozoa and amœbæ, nematodes and the like, have been shown to play an important part in determining the activity of the lower organisms and therefore the fertility of the soil. A large amount of work has been done in the way of isolating and describing particular organisms present in the soil, but for practical purposes it is less important to identify species than to ascertain the collective activity of groups of organisms which possess the same function. Many efforts have been made to measure the activity of these various groups so as to obtain a quantitative estimate of the factors which determine the preparation or destruction of plant foods, but it cannot be said as yet that the methods devised are satisfactory, or have received general acceptance as leading to results which can be correlated with the fertility of the soil when determined by the yield of test plots.

The soil bacteria may be conveniently grouped under the following heads:—

(a) Humus-making organisms which transform carbohydrates and other plant residues into humus.

(b) Nitrogen-fixing organisms which are capable of taking up free gaseous nitrogen and bringing it into combination in the material of which their own cells are composed.

(c) Ammonia-making organisms which attack the proteins and other less complex compounds of nitrogen and break them down with formation of ammonia.

(d) Nitrifying organisms which oxidise ammonium compounds and give rise to nitrites and nitrates.

(e) Denitrifying organisms which reduce nitrates to nitrites and to free nitrogen gas. In this group are generally included a further set of organisms, probably distinct, which set free nitrogen gas from organic compounds of nitrogen.

In addition to these main groups there are other organisms which sometimes play an important part in the soil, for example, the reducing organisms which form sulphides, hydrogen sulphide, and free sulphur from sulphates, and the iron organisms which secrete hydrated ferric oxide from solutions containing ferrous carbonate.

1. The relative predominance of organisms of the bacterial or fungoid type seems to be determined by the reaction of the soil. In

neutral or very slightly alkaline soils, bacteria predominate; in acid soils, micro-fungi are chiefly active; and many important groups of bacteria, such as those bringing about nitrogen fixation and nitrification, may be entirely absent.

For the determinations of the number of organisms present in the soil, and indeed for all determinations of bacterial action, special samples must be taken.

A thin brass tube about 1 in. in diameter, sharpened at the lower end like a cork borer, is forced into the soil to a depth of 6 ins., then placed in a sterilised glass tube plugged with cotton wool for removal to the laboratory.

Another method which is more convenient, as yielding samples from various depths, begins by the construction of a special boring tool which can be driven into the ground. The tool consists of two strips of steel, $\frac{1}{8}$ in. in thickness, 8 ins. long and 2 ins. wide, each bent down the whole length of the strip so as to form two wings, 1 in. wide, at right angles to one another. The edges are then bevelled off until the two pieces of steel can be put together so as to form a box, 1 sq. in. in section and 8 ins. long, in which position the pieces are retained by steel rings which can be forced over the two ends. The lower end of the tool is sharpened and it is then driven into the soil to the required depth of 6 ins. After removal, the rings can be knocked off, whereupon the box falls apart showing a square core of soil, any portion of which can be taken. In the laboratory the soil, still in a moist condition, is carefully broken down with a spatula and is worked through a sieve with holes 3 mm. in diameter. Two portions of 25 grms. are weighed out, one is dried to determine the water content, the other is shaken up for about 5 minutes with 250 c.c. of sterile physiological salt solution, containing 0·5 p.c. sodium chloride and 0·2 p.c. of magnesium sulphate. From this turbid liquid, 1 c.c. is pipetted off and added to another flask containing 99 c.c. of similar sterile salt solution. After well shaking 1 c.c. from this dilution is again transferred to a further 99 c.c. of sterile salt solution, and after again shaking 1 c.c. of this last dilution is added to a test tube containing 10 c.c. of nutrient gelatine, and the plate poured in the usual way. The plates are incubated for 8 days at a temperature of 20°; each plate represents 0·0001 gram of soil in its moist state. The gelatin medium usually employed contains 1 p.c. of beef extract, 1 p.c. of peptone, and 0·5 p.c. of sodium chloride with 10 to 12 p.c. of gelatin. A gelatin medium has the advantage of showing the liquefying organisms, of which a separate count can be made; humus-making organisms can also be distinguished by the furry appearance of the colonies or even by the formation of a brown ring, but the gelatin has the disadvantage of inhibiting a number of organisms which do not develop in the presence of much organic nitrogen. In place of the gelatin, 1·5 p.c. agar may be used; but though the agar plates permit of the growth of other organisms, they do not distinguish between liquefying and non-liquefying organisms, and many motile organisms work about the surface and may obscure the results or give rise to secondary colonies. Another

useful medium is soil-extract agar made up as follows: Equal quantities of water and soil are boiled for half an hour and filtered, the liquid being further filtered through a Chamberland filter to get a clear extract. To the extract, 1 p.c. peptone and 1 p.c. dextrose or 1 p.c. dextrose alone are added, and the jelly is made up with $1\frac{1}{2}$ p.c. agar as usual. This medium, without peptone, will permit of the growth of the nitrogen-fixing organisms, though it will inhibit the putrefactive, ammonia-splitting, and other organisms dependent upon combined nitrogen.

Another method of determining the collective action of the bacteria of the soil has been devised by Russell (J. Agric. Sci. 1905, 1, 261). He determines directly the oxidising power of the soil and finds it correlated with its fertility. The apparatus consists of a bulb of about 100 c.c. capacity with two tubes sealed into its neck, one of which is a long narrow tube dipping into mercury and constituting a gauge, while the other expands into a small flask partly filled at the beginning of the experiment with a solution of potash. 10 grms. of air-dried soil are placed in the flask with 2 c.c. of water, the flask is then sealed up and placed in a water-bath maintained at a constant temperature of about 20°. The apparatus is left for several days, whereupon the oxygen contained in the enclosed air is slowly converted into carbon dioxide which is absorbed by the potash, resulting in the diminution of the pressure of the enclosed air. Finally, the rate of oxidation is determined by the reduction in pressure which has taken place. It is necessary to make comparative trials with soils whose behaviour in the field is known, and while no absolute value can be given to the results, they are valuable as measuring the gross rate of bacterial activity in the soil and as supplying valuable indications of its fertility.

2. *Humus-making organisms*.—The decay of organic matter in the soil seems to proceed in two distinct fashions; in the presence of air the organic matter is broken down by micro-organisms of all kinds with the eventual production of carbon dioxide, water and ash. On the other hand, if the decay takes place under conditions which exclude oxygen, the process is more limited; carbon dioxide, marsh gas, hydrogen and other compounds are produced and there is left behind a black material containing more carbon but less oxygen and hydrogen than the original vegetable matter. Both aerobic and the anaerobic decay gives rise to brown or black humus compounds, but it is not certain whether the same organisms take part in both processes or which predominate under ordinary soil conditions of partial exclusion of oxygen. The anaerobic processes have been studied in some detail, and Omelianski has isolated two organisms which are capable of attacking carbohydrates like cellulose. In one case, the products are carbon dioxide, hydrogen, various organic acids, and humus; and the other, which is perhaps the more general, carbon dioxide, methane, butyric and other organic acids, are produced. The process may be readily illustrated by filling a flask with a nutrient solution containing 0.1 p.c. KH_2PO_4 , 0.1 $(\text{NH}_4)_3\text{PO}_4$, 0.05 MgSO_4 , and a trace of NaCl , and introducing strips of filter paper with a small

quantity of soil, or better still of pond mud. The flask is closed with an exit tube dipping down into water. After some days' incubation at 34°–35°, the filter paper will begin to disintegrate, at the same time gas will be given off consisting of a mixture of carbon dioxide, nitrogen, methane, and sometimes hydrogen. An aerobic organism which presumably plays the more important part in ordinary soil conditions has recently been isolated and investigated by Hutchinson and Clayton (J. Agric. Sci. 1919, 9, 143). This organism (*Spirochaeta cytophaga*) exists in two forms, as a sinuous filamentous cell, feebly motile, and a spherical sporoid. The organism does not grow on ordinary gelatine or agar preparations, and does not utilise other carbohydrates than cellulose, indeed is inhibited by them. Its nitrogen requirements may be met by any of the simpler nitrogen compounds—ammonium salts, nitrates, &c. From the cellulose are produced a yellow pigment, small quantities of volatile acids, a mucilage which does not give rise to optically active compounds on hydrolysis, but no gas. Humus may be either acid (as in peat soils), or neutral when it is formed in the presence of calcium carbonate, as is usual in soils.

Nitrogen-fixing organisms.—The first demonstration that the soil contains bacteria capable of bringing gaseous nitrogen into combination was due to Hellriegel and Wilfarth in 1886, who showed that the small nodules which may be found upon the roots of clover, beans, and other leguminous plants contain colonies of bacteria living symbiotically with their host plant, deriving from it the carbon compounds which they need, and handing over nitrogen which they have 'fixed' from the atmosphere with which the plant roots are in contact. It was found that clover and other plants possessing such nodules upon their root do become richer in nitrogen and that in practice the soil is markedly enriched by their growth. Such gains in nitrogen only take place when the seedling plant can become infected either by growing in soil which normally contains the organism, or by addition to a sterile soil of either the extract from a nodule of some infected plant or a trace of normal soil. To the organism the name of *Pseudomonas radiculicola* has been given, and further investigation has shown that while only one general species can be distinguished it has, to a certain extent, been specialised by association with particular plants. Thus better results are obtained when beans are inoculated with the organism derived from a nodule of a bean plant than with organisms from a lupin plant, and in some cases (lupins and lucerne) this specialisation has proceeded so far that the plant is only very slightly infected by the neutral form of the organism which exists in ordinary soil. In the soil, the organism appears to exist in minute rod-shaped organisms in rapid motion which infect the plant by passing through the cell walls of the root hairs. Inside the plant, the organism first of all develops into much larger rod-shaped organisms, which finally become, in the nodules, characteristically bent or Y-shaped organisms known as bacteroids. It is possible to cultivate *Pseudomonas radiculicola* on the non-nitrogenous media described above, as, for example, soil-extract dextrose, agar-agar,

but the fixation of nitrogen under these conditions is inconsiderable.

From time to time, soils are found, the commonest example being peats and heaths of an acid reaction, in which *Pseudomonas radiculicola* is not present, and when these soils are brought into cultivation, leguminous plants do not at first develop nodules and fix nitrogen. In this case, it may be desirable to proceed to an inoculation of the soil which, however, must first be rendered a suitable medium for the development of the organisms by the removal of its acidity and the addition of lime and phosphates. One method of effecting the inoculation is to strew over the field about $\frac{1}{2}$ ton to the acre of soil taken from a cultivated field on which the leguminous plants have been growing normally. Another method is to prepare an active culture of organisms from a nodule of the crop it is desired to sow, and with this prepare a large bulk of sub-culture by introducing it into ordinary tap water in which $\frac{1}{10}$ p.c. of dextrose and $\frac{1}{100}$ p.c. potassium phosphate have been dissolved. Into the large bulk of crude culture thus obtained after standing two or three days, the seed, tied up in a thin muslin bag, is dipped and allowed to dry somewhat before sowing, when it will be found to carry with it sufficient organisms to ensure inoculation. As a rule, the leguminous crop still grows rather indifferently after its first inoculation, and only really flourishes when grown for a second or third time after the organism has established itself in the soil. Many attempts have been made to improve the growth of leguminous crops in ordinary soil by inoculating them before sowing, but, except in the special cases just mentioned, no success has attended the process. Amongst ordinary farm crops, the only call for inoculation appears to occur with lucerne when attempts are made to grow this plant on soils which have not hitherto carried it, since lucerne does not seem to be readily infected by the neutral form of organism, such as that left by the clover which may have been regularly grown on the same soil previously. Since the discovery of *Pseudomonas radiculicola*, other organisms have been discovered living free in the soil which are capable of bringing nitrogen gas into combination. Winogradsky isolated from pond mud and other similar material under anaerobic conditions a widely diffused organism called *Clostridium pastorianum* which breaks down carbohydrates with the formation of humus, butyric acid, &c., accompanied by the fixation of a small amount of nitrogen—two to three mgm. for each gram of carbohydrate destroyed. The most important of the nitrogen-fixing organisms, however, is one discovered by Beijerinck, named by him *Azotobacter chroococcum*, which as such or as one of its closely allied forms has been isolated from soils in nearly all parts of the world. Its presence can be readily determined by adding a small portion of soil to 50 c.c. of sterile culture fluid containing per litre 10 grms. of mannite or glucose, 0.2 gm. each of potassium phosphate, magnesium sulphate, and sodium chloride, and 0.1 gm. of calcium sulphate and a trace of ferrous sulphate. The solution is placed in a small Erlenmeyer flask, $\frac{1}{2}$ gm. of calcium carbonate added, the flask is plugged

and its contents sterilised. After adding the soil the flask is placed in an incubator at 25° for a week, by which time a considerable fermentation will be found to have taken place accompanied by the evolution of carbon dioxide and the formation of a brown scum upon the surface of the liquid. *Azotobacter* is a powerful oxidising organism, converting the carbohydrate into carbon dioxide and water, together with small quantities of lactic and acetic acid, alcohol and sometimes butyric acid. At the same time about 9 to 10 mgs. of nitrogen are fixed for each gm. of carbohydrate oxidised. *Azotobacter* is a large oval organism, 4 to 5 μ in length and 3 μ in width. It differs from most bacteria in containing glycogen, so that it stains a deep brown colour with a solution of iodine. *Azotobacter* is not found on acid soils, the presence of calcium carbonate is essential to its development; to it and kindred organisms must be attributed a large share of the formation and maintenance of the stock of nitrogen contained in soils. Particularly to this agency do we look to explain the formation of the deep black soils of the Russian Steppes, the American North-West, Argentina, &c. It is, however, essential that the organism shall receive a supply of carbohydrate, by the oxidation of which it obtains the energy required to bring gaseous nitrogen into combination. At Rothamsted, it has been shown that the soil of the wheat field, from which the whole crop with the exception of a small quantity of roots and stubble is removed, gains very little nitrogen by bacterial agency, although the *Azotobacter* is present in the soil. An adjoining piece of land, however, on which the débris of grass and other wild vegetation fall back to the soil and is not harvested, there have been accumulations of nitrogen at a rate approaching 100 lbs. per acre per annum over a period of 25 years, and this case is parallel to the formation of the virgin soils above mentioned.

3. *The ammonia-making organisms.*—As a group the ammonia-making organisms have not received much study, although recently it has been shown that the fertility of the soil must be largely determined by their activity. The greater number of the organisms found in the soil—the organisms, for example, which grow upon gelatin plates including such well-known putrefactive organisms as *Proteus vulgare*, *Bacillus mycoides*, *B. mesentericus vulgatus*, *B. subtilis*, *Bact. fluorescens liquefaciens*, *B. coli*, &c., must belong to this group. Their general function is well known; they are capable of attacking proteins and resolving them successively into a lower form of combination, amino-acids, &c., until at last the nitrogen reaches the state of ammonia. In addition the soil contains other organisms not capable of dealing with the proteins, but resolving the simpler nitrogen compounds into ammonia. Of these the best known are the urea-splitting organisms, *Micrococcus ureæ*, *Urobacillus pasteurii* and *Planosarcine ureæ*, which hydrolyse urea with formation of ammonium carbonate and water. These organisms which are exceedingly abundant in stables, cow stalls, &c., are also present in the soil. The dependence of the fertility of the soil upon the numbers of the ammonia-making organisms has been made evident by the work

of Russell and Hutchinson (J. Agric. Sci. 1909, 3, 111) on the effects of partially sterilising soil by heat or by exposure to the vapour of antiseptics like chloroform, toluene, &c. These investigators found that a soil which had been heated to a temperature of 100° for 2 hours and then placed under normal conditions favourable to growth gave rise to a much increased crop, the yield being in many cases doubled, while the amount of nitrogen in the plant became three or four times as great as that on the untreated soil. This increased crop was found to follow to a large extent the rate of the formation of ammonia in the soil, the ammonia in this case being taken up as such by the plant, because the nitrifying organisms had been destroyed. It was also found that the soil was not completely sterilised by the processes; the spores of certain groups resist the heat and develop to an unprecedented extent when the soil was once more placed under conditions favourable for growth. For example, a normal soil is found to contain about 8 million bacteria per gram before being subjected to treatment, and this number remained comparatively constant under ordinary conditions of growth. After heating the number of organisms per gram was reduced to as few as 60, but they increased rapidly from day to day when the soil was moistened and placed in the incubator, until in a fortnight's time they amounted to 40 millions or over per gram. The increase in fertility proceeded *pari passu* with the increased rate of production of ammonia, which in its turn depended on the increase in the number of organisms.

It was evident from the experiments that the heating had removed a factor present in ordinary soil which inhibited the development of the bacteria beyond a certain point, and it was found that the untreated soil contained a number of large organisms—protozoa, amœbæ, &c., which derive their sustenance from living bacteria. Under normal conditions an equilibrium exists between the numbers of these larger organisms and of the bacteria, and as the heating process kills off the larger organisms entirely while still leaving some of the bacteria, the latter can develop to a hitherto unprecedented extent in the absence of the factor which previously kept them in check. Exposure of the soil to the vapour of chloroform, toluene, &c., for 48 hours, followed by its complete evaporation, has the same effect in destroying the larger organisms while leaving a certain number of the bacteria or their spores ready to develop as soon as conditions favourable to growth are obtained. With these volatile antiseptics, however, destruction of the larger organisms is not so complete nor the gain of fertility so large. It has not yet been found possible to apply these processes of partial sterilisation to increasing the fertility of soils in the open, but a commercial process has been successfully worked out for greenhouse soils, which, owing to their conditions of richness in manure, high temperature and water content, afford a specially favourable medium to the development of the larger organisms.

4. *Nitrification*.—The process of nitrification and the factors by which it has been governed have long been worked out in a practical way.

For example, in the *Instruction sur la fabrication du nitre: Par les régisseurs Généraux des poudres et salpêtres*, 1777, the formation of nitre beds is carefully described. They were made up of earth containing a certain amount of calcareous matter, mixed with dung and other nitrogenous residues. They were protected from the weather and carefully watered from time to time with diluted urine and other materials containing nitrogen. After two or three years, the contents of the bed were lixiviated, and the solution of calcium nitrate obtained was concentrated and treated with potassium sulphate, whereupon potassium nitrate could be crystallised out of the clarified mother-liquors. It was thus recognised that soil is capable of converting organic compounds of nitrogen into nitrates in the presence of a base like calcium carbonate, and that warmth and a certain proportion of moisture are factors favourable to the process.

That the process was due to a living agency was first demonstrated by Schloesing and Müntz in 1877. These investigators showed that the action ceased if the soil was heated to the temperature of boiling water or was kept in contact with vapour of chloroform and similar antiseptics, and further that it only took place between the temperatures of 5° and 55°.

Warington, who continued the investigation, further showed that there are two stages of the oxidation process, one being the formation of nitrite followed by its oxidation to nitrate. Cultures were obtained capable of effecting one only of these changes, but owing to the difficulties of growing the organisms on the ordinary gelatin medium, it was not until Winogradsky, in 1890, devised a medium of silica jelly containing no combined nitrogen that the organisms were finally isolated in a pure state. Winogradsky obtained from soils in all parts of the world a single organism which he called *Nitrobacter*, capable of transforming nitrites into nitrates, but he obtained two organisms, *Nitrosomanas europea* in the soils of the old world, and a second *Nitrococcus javanensis* from the soils of Java, America, and Australia, which will transform ammonia into nitrites. The conditions of the activity of these organisms appear to be the absence of excess of organic matter, a neutral or faintly alkaline medium with some base in reserve to combine with the nitric acid produced, and the absence of any excess of alkaline carbonates or chlorides. It has been found possible to accustom the organism by successive cultivations to a toleration of ammoniacal and organic solutions much stronger than would normally inhibit its development. The organism derives the carbon necessary to its growth from carbonates in the culture medium or carbon dioxide in the air with which it is supplied. The nitrifying organisms are confined, as indeed are all bacteria, to the surface layers of the soil, being rarely present in subsoils at greater depth than 2 ft. They may be entirely absent from the soils of heaths or peaty bogs which are acid in their reaction, but are abundant in waters of shallow wells and rivers. Their development is promoted by warmth, by stirring the soil, and by free aeration. It was formerly considered that as the higher plants obtain their combined nitrogen almost

entirely in the form of nitrate, the fertility of the soil must be determined by the activity of the nitrification process going on in it, but it is now considered that the nitrification process is only the end term of the oxidation of organic compounds of nitrogen, and that it proceeds as rapidly as ammonia can be supplied by the ammonia-making organisms above described. It is found, for example, that ammonia never accumulates as such in normal soils, whereas nitrates do. Thus the activity of the ammonia-making organisms is the factor determining the rate of production of nitrates, and therefore the fertility of the soil.

5. *Denitrification*.—It was observed by Warington that when a soil containing organic matter and sodium nitrate was water-logged so as to deprive it of air, there was a considerable development of nitrogen gas accompanied by a loss of nitrogen to the soil. Gayon and Dupetit isolated two organisms from sewage which would reduce nitrates to nitrogen gas in the presence of organic matter, the action being chiefly carried on when oxygen was absent, but coming to a standstill when plenty of air was supplied so that the organism had no need to attack the nitrates in order to obtain oxygen. This property of reducing nitrates in the absence of free oxygen has since been found to be common to a large number of organisms. To the process the name of denitrification has been given, and it explains the fact observed in many experiments, particularly in pots, that when large quantities of organic manure like dung are used in conjunction with sodium nitrate, smaller returns are obtained than when either of the fertilisers is employed singly. In ordinary field practice, however, losses of this kind are hardly to be feared, because the soil rarely becomes sufficiently rich in active organic matter, nor so sealed from the access of air, as to lead to any attack upon the nitrate. At Rothamsted, for example, it has been found with the mangold crop that of the nitrogen applied as sodium nitrate, 78 p.c. is recovered when no organic or other nitrogenous manure is applied, while 61 p.c. is recovered when the nitrate is added to a plot which also receives dung at the rate of 14 tons per acre per annum, the recovery being reckoned on the excess of crop over that produced by dung alone. The lower recovery, when nitrate is used in connection with dung, is no more than might be normally expected under the law of diminishing returns. In certain circumstances, however, as in rice growing on water-logged soils containing much organic matter, it is inadvisable to apply sodium nitrate because of the denitrification that takes place. To denitrification consequent on water-logging rather than to leaching may probably be attributed the loss of nitrates and consequent infertility of the heavier types of soils after a wet winter. The term 'reduction' is also more loosely applied to the loss of gaseous nitrogen which takes place whenever soils are brought into very high condition by excess of organic manures. There exist in the soils various groups of bacteria destroying organic matter with evolution of nitrogen gas, and the activity of the organisms increases with the amount of organic matter with which the soil is supplied. Thus a very highly manured soil tends

to reach a condition of equilibrium in which the supply of nitrogen is balanced, in part, by the output of crop, but also by the accelerated activity of the organisms setting free nitrogen gas. For example, on the wheat field at Rothamsted, to which dung is applied at the rate of 14 tons per acre per annum, it has been found that during the 50 years, 1844–93, of the 200 lbs. of nitrogen annually applied, only about 26 p.c. was recovered in the crop and 25 p.c. was accumulated in the soil. Thus nearly 50 p.c. was wasted, and though some of it would have been removed by drainage water as nitrates, the greater part has been dissipated as nitrogen gas formed by bacterial action in the very rich soil. The condition of water-logging which leads to denitrification may also be accompanied by the reduction of sulphates and the formation of black ferrous sulphide in ordinary soils. For the bacteria of sulphate reduction and other sulphur organisms, also for iron organisms, *v. Russell, infra*.

The great extent of the literature existing on soil organisms precludes the setting out of references, but further details, together with a full bibliography, may be found in Russell ('The Micro-organisms of the Soil,' Longmans, 1923).

For the toxicity and antagonism of various alkali salts in soils, *see* Harris, Thomas and Pittman (J. Agric. Res. 1923, 24, 317).

See also Microbiological analysis of soil as an index of soil fertility, III. Influence of fertilisation upon the number of micro-organisms in the soil (S. A. Waksman, Sol. Sc. 1922, 14, 321–346; J. Soc. Chem. Ind. Abs. vol. 42, 1923, p. 237). *See also* Waksman and Starkey (Sol. Sc. 1924, 17, 141; Chem. Soc. Abstr. 1924, i. 818; Waksman and Henkelekian, Sol. Sc. 1924, 17, 275; Chem Soc. Abstr. 1924, 126, i. 928).

A. D. H.

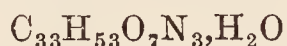
SOJA BEAN OIL *v.* SOYA BEAN OIL.

SOLANIDINE *v.* SOLANIN.

SOLANINE. This name was first applied by Desfosses (B. J. 1820, 2, 114) to a base isolated from *Solanum nigrum* (Linn.), and subsequently from *Solanum Dulcamara* (Linn.), and, later on, from other solanaceous plants, including potato and tomato plants. The composition and the homogeneity of solanine from different sources have not yet been ascertained beyond doubt, but it seems likely, as Firbas has stated (Monatsh. 1889, 10, 541), that at least two substances of this type are present in these various plants, *viz.* *solanine* and *solaneine*, and these may be accompanied by *solanidine*, a basic decomposition product of solanine. All authorities are agreed that solanine is an alkaloidal glucoside, but there is good reason to believe that the substances from different plants that have been named solanine are not all identical. The principal recent papers referring to solanine and the related substances are by Cazeneuve and Breteau, Compt. rend. 1899, 128, 887; Schulz, Zeit. Zuck-Ind. Böhm. 1900, 25, 89; Sage, Pharm. J. 1902, [iv.] 14, 174; Davis, *ibid.* 1902, [iv.] 15, 160; Oddo and collaborators, Gazz. chim. ital. 1905, 35, i. 27; 1906, 36, i. 310; 1911, 41, i. 490; Atti R. Accad. Lincei. 1906, [v.] 15, ii. 312; 1907, [v.] 16, ii. 683; Wittmann, Monatsh. 1905, 26, 445; Romeo, Gazz. chim. ital. 1905, 35, ii. 579. Oddo deals chiefly with solanine-S ($C_{27}H_{46}O_9N$) $_2H_2O$, m.p. 275°–280°, from *Solanum*

sodomœum tubers, which he regards as distinct from potato-solanine $C_{32}H_{51}O_{11}N$, m.p. 262°.

Tutin and Clewer (Chem. Soc. Trans. 1914, 105, 564) have isolated *solangustine*



from *Solanum angustifolium*, used in South America as a febrifuge. On hydrolysis it yields an amorphous base *solangustidine*, $C_{27}H_{43}O_2N$, which forms a number of well-crystallised salts. The formula of solanine from potatoes is very doubtful ($C_{28}H_{47}O_{10}N?$; $C_{52}H_{93}O_{18}N?$). On hydrolysis with dilute acids *d*-galactose, rhamnose and possibly a disaccharide are formed (Votoček and Vondraček, Ber. 1903, 36, 4372; Zeisel and Wittmann, *ibid.* 1903, 36, 3554). The other product *solanidine* ($C_{40}H_{61}O_2N?$ Firbas, Wittmann) crystallises from alcohol in long silky needles. Solanine is best obtained from potato shoots up to 4 ins. long, formed by sprouting in the dark. The use of acids must be avoided. Unpeeled potatoes contain 0.0078–0.0116 p.c., peeled ones 0.0040–0.0066 p.c. (Meyer, Arch. exp. Path. Pharm. 1895, 36, 361). Von Morgenstern (Landw. Vers. Stat. 1907, 65, 300) found an average of 0.0125 p.c. in 18 varieties intended for human consumption. The physiological properties of solanine have been investigated by Schmiedeberg (Arch. exp. Path. Pharm. 1895, 36, 373).

Potatoes rich in solanine when eaten occasion burning and itching in the throat, nausea and retching; such potatoes have a bitter taste.

The amounts of solanine in suspected potatoes may be estimated by the following process due to Bömer and Mattis (Zeitsch. Nahr. Genussm. 1923, 45, 288–291; *ibid.* 1924, 47, 97; Chem. Soc. Abstr. 1924, i. 813, 814). About 200 grms. of the ground-up potatoes are mixed with 250 c.c. of water, and the mass expressed after some time. The residue is then digested for 30 minutes with three successive portions of 250 c.c. of water acidified with 5 drops of acetic acid, and expressed after each digestion. The united pressings are rendered slightly alkaline with ammonia and evaporated to dryness with 10 grms. of kieselguhr, and the dry residue powdered and extracted for 5 hours with 95 p.c. alcohol in a Soxhlet extractor, the residue being then ground up and again extracted for 5 hours. The total extract is evaporated, the residue dissolved in water acidified with a few drops of acetic acid, the solution made slightly alkaline with ammonia and heated on the water bath, and the flocculent precipitate of solanine filtered off and washed with warm 2.5 p.c. ammonia solution. Finally, the solanine is purified by dissolving it in alcohol, filtering the solution, evaporating the filtrate and treating the residue as described above, and the final colourless residue is collected on a weighed filter. Three normal varieties of potatoes of different kinds contained 2.0, 2.1, and 7.5 mgrms. of solanine in 100 grms. of potatoes, whilst six suspected samples gave the following results: (1) 57.8 and 58.8; (2) 50.5; (3) 37.6; (4) 43.4 and 41.2; (5) 26.1 and 25.3; and (6) 32.9 mgrms. per 100 grms. (Analyst, 1923, 48, 454).

It appears possible that the formation of solanine in such large proportions is due, to some extent, to the action of light (*cf.* Analyst,

1918, 43, 133). See also Schowalter and Hartmann (Zeitsch. Nahr. Genussm. 1924, 47, 251; Analyst, 1924, 49, 394).

The cause of some mild cases of poisoning was traced by G. Griebel to two consignments of potatoes containing abnormally large proportions of solanine. The two consignments came from different neighbourhoods, but appeared to be of the same variety. These appear to be the first cases of solanine poisoning which have occurred from the consumption of potatoes in December, immediately following the harvest. In one case the content of solanine in the potatoes reached 0.79 p.c. (0.555 p.c. in the peeled potato), which is the highest figure so far reported for sound potatoes. The evidence as to the cause of the high content of solanine in potatoes is not complete, but exposure to light appears to have a certain influence on the formation of solanine in the potato (G. Griebel, Zeitsch. Nahr. Genussm. 1923, 45, 175–183; J. Soc. Chem. Ind. 42, 1923, 903 A. See also Art. POTATO, vol. v. p. 404). G. B.

SOLANUM MELONGENA, L. The egg plant. The egg plant contains water, 95.5 p.c. and dry substance 4.5 p.c., the latter containing total nitrogen 5.089 p.c., protein nitrogen 3.71 p.c., and non-protein nitrogen 1.379 p.c. The aqueous extract contains trigonelline 0.025 p.c., 4- β -amino-ethyl-glyoxaline 0.003 p.c., and choline 0.034 p.c., calculated on the undried substance (Yoshimura, J. Chem. Soc. Japan, 1921, 42, 16).

SOLARGENTUM. Silver Gelatin.

SOLARSON. Ammonium Salt of hepten-chlorarsenic acid.

SOLDERS. Solders consist of fusible alloys, which are used for joining metals together and are of various kinds depending on the nature of the metals to be joined. They are distinguished by specific names, as hard-, soft-, white-, spelter-, silver-, gold-, aluminium-, copper-, tin-, plumbers'-, pewterers'-, and button-solder, &c. For whatever purposes they may be intended they should always be rather more fusible than the metal or metals to be united; and, to give the maximum strength, they should have about the same hardness and malleability as these metals. Solders may be divided into two classes, *hard* and *soft solders*.

Hard solders are commonly called *spelter* (a name which is also in technical use for cast zinc). Hard soldering is usually termed *brazing*, since the solders most commonly employed are similar to brass in composition. Brazing is used where greater strength is required than can be given by soft solder, or when an article has to stand a temperature that would cause soft solder to melt. Hard solders contain such metals as copper, silver, &c., and require a red heat to fuse them. The heat necessary is derived from either a forge fire, a benzoline or paraffin brazing lamp, or a brazing hearth, which is an arrangement of gas blowpipes (*v.* J. Soc. Chem. Ind. 1902, 21, 259). A brazed joint is commonly considered to be stronger than the adjacent metal, and is generally cheaper, easier, simpler, and quicker to make than a welded joint.

Soft solders are composed of lead and tin in varying proportions; sometimes bismuth is added. The following table (Tomlinson) of

melting-points of a series of lead-tin alloys shows that soft solders melt below 300°; numbers 4 to 8 represent common solders:—

TIN-LEAD SOLDERS.

No.	Tin	Lead	Melting-point	No.	Tin	Lead	Melting-point
1	1	25	292°	7	1½	1	168°
2	1	10	283°	8	2	1	171°
3	1	5	266°	9	3	1	180°
4	1	3	250°	10	4	1	185°
5	1	2	227°	11	5	1	192°
6	1	1	188°	12	6	1	194°

The addition of bismuth lowers the melting-point; by varying the proportions of the constituents such alloys may be made, within certain limits, to melt at any desired temperature, even below 100°, thus admitting of various applications for electrical and other purposes. Examples are shown in the following table:—

BISMUTH SOLDERS.

Parts of tin	Parts of lead	Parts of bismuth	Melting-point	Parts of tin	Parts of lead	Parts of bismuth	Melting-point
3	5	3	94.4°	1	1	1	123.3°
1	1	2	96.1°	2	2	1	143.5°
1	2	2	112.8°	3	3	1	154.4°
2	1	2	113.3°	4	4	1	160.0°

Soft solders are usually weaker in tensile strength than the joined metals.

Although soft solders are sometimes employed in conjunction with a mouth blowpipe, they are usually applied by means of a suitably shaped copper bit, miscalled a soldering iron.

In preparing solders, care must be taken to avoid two faults, want of uniformity and loss of a constituent that is either volatile or readily oxidised. Thus where copper, silver, &c., are to be mixed with tin, zinc, &c., it is necessary to melt the least fusible metal first; the zinc or tin is finally added, and after stirring, the mass is quickly cast. Efficient stirring, preferably with a piece of green wood, is necessary to secure uniformity of composition. Soft solders should be melted under tallow; they are cast in sticks, or run out into strips. Hard solders should be melted under powdered charcoal or borax. They may be granulated, or cast into small ingots and reduced to powder by filing. Gold and silver solders are generally rolled out into thin sheets and cut into narrow strips or else drawn into thin wire.

In the practical application of solders it is necessary that the metal surfaces to be united should be heated to a temperature above that at which the solder melts, and that the surfaces should be bright and clean, both mechanically and chemically. They may be cleaned mechanically by scraping or filing, and chemically by washing with a suitable acid or alkali. Since most metals tarnish when heated, owing to surface oxidation, it is necessary to protect the metal surfaces from air during the period of heating, or the solder will not wet the metals and adhere to them. Hence the use of *fluxes* in soldering. The flux used in hard soldering is *borax*. For soldering small articles, it may be prepared for use by rubbing a lump with water on a clean slate to a creamy consistency, and is then applied to the surfaces with a brush. When heated, the water is first expelled; at a red heat

the anhydrous borax melts, and, flowing over the surfaces, it not only prevents access of air but also dissolves any surface films of oxides, producing double metaborates which remain dissolved in the excess of borax. It has been proposed to carry out brazing in an atmosphere of hydrogen or carbon monoxide (*J. Soc. Chem. Ind.* 1911, 30, 695).

Soft solders melt at temperatures below the fusing-point of borax, and other fluxes are therefore necessary. *Zinc chloride* solution is commonly used with most sheet metals, brass, copper, gun-metal, and bright iron. *Hydrochloric acid* is used with zinc and galvanised ware; *ammonium chloride* with copper and iron; *resin* with soft alloys and tinware; *Venice turpentine* or *Gallipoli oil* with pewter or Britannia metal; *Russian tallow* with heavy lead and *palm-oil candle* with light lead work. Lactic acid 1 pint, glycerol 1 pint, water 8 pints makes a good flux, as also does a solution of phosphoric acid in alcohol.

Resin possesses an advantage over acid fluxes like hydrochloric acid or zinc chloride as it does not induce subsequent corrosion. All excess of an acid flux should be thoroughly washed away. When it is necessary to use soft solder for repairing jewellery, resin cannot be used as it spreads all over the surfaces and is difficult to remove; zinc chloride should be used. The common prejudice against using zinc chloride when soldering electrical joints is stated by Lippmann to be groundless (*Zeitsch. angew. Chem.* 1909, 22, 2042). For a comparison between several fluxes, *v. Samter (ibid.* 1909, 22, 729).

Soft solders can be obtained in the form of narrow bore-tubes, with the central portion filled up with resin or other material, so as to obviate the necessity for using a separate flux. They may also be obtained, mixed with flux, in the form of a paste, *e.g.* (1) granulated soft solder is mixed with beeswax and impregnated with zinc chloride (*J. Soc. Chem. Ind.* 1906, 25, 269); (2) powdered solder is mixed with borax, ammonium chloride or other flux that leaves no acid residue and incorporated with glycerol or other inert and not too volatile substance (*ibid.* 1905, 24, 32); (3) powdered tin or solder is mixed with zinc chloride and celluloid paste and applied with a brush (*ibid.* 1903, 22, 1052).

For practical details of the art of soldering and descriptions of the requisite apparatus, consult books on metal working, Rowell's *Hard Soldering*, and Hobart's *Brazing and Soldering*.

Hard solders. *Gold solders.*—Articles the fineness of which varies from 14 to 22 carats, may be soldered with alloys of lower grade prepared by fusing 2 grs. of silver and 1 gr. of copper with 1 pennyweight of gold of the same fineness as the article. These alloys are used in *dental* work. By replacing the 3 grs. of silver and copper by an equal weight of spring brass (2 of Cu, 1 of Zn), solders of good colour are obtained, suitable for use with *ornaments* and *jewellery*.

Coin gold is usually soldered with an alloy of pure gold 3 parts, spring brass 1 part.

Gold of a fineness of 12 carats or less may be soldered with 10 or 12 carat gold to which one-twelfth of its weight of zinc has been added. A gold solder should not contain less than one-

third its weight of gold. Lower grades of gold are best soldered with silver solder.

A good solder for *general use* contains gold 18, silver 4, copper 5, zinc 2 parts ; another can be readily prepared by fusing 1 pennyweight of 18 carat gold with 5 grs. of spring brass. Among other jewellers' gold solders, the following may be mentioned ; (1) best solder, gold 12½, silver 4½, copper 3 parts ; (2) medium solder, gold 10, silver 6, copper 4 parts ; (3) common solder, gold 8½, silver 6½, copper 5 parts ; *v. Gee*, The Goldsmith's Handbook.

Antimony, arsenic, tin and lead should not be used in solders for gold.

Silver solders.—These are largely employed in the arts ; owing to the careful, sparing way in which they are used, most work requires but little finishing after soldering. The use of silver solders is not therefore unreasonably expensive ; the results are extremely satisfactory. Besides being employed by jewellers and silversmiths, silver solders are also used for joining brass, copper, and even iron and steel.

Hard solders for *jewellers* and for *general use* contain : (1) silver 18, copper 4, zinc 1 part ; (2) silver 15, copper 4, zinc 1 part. A good solder may be prepared by melting coin silver and adding one-third its weight of spring brass. An easy melting solder is prepared by fusing 2 parts of fine silver and adding 1 of spring brass, or by employing silver 4, copper 1, zinc 1 part, while an alloy of silver 16, zinc 1 part forms a very hard, white solder. A very common solder contains silver 1, brass 1, arsenic 1 part.

Many other silver solders are in use. A selection is given in the accompanying table, with remarks upon their uses. *See also Gee*, The Silversmith's Handbook.

SILVER SOLDERS.

Remarks on use	Parts of silver	Parts of spring brass	Parts of copper	Parts of zinc
Jewellers', hardest	4	—	1	—
" hard	16	—	3·5	0·5
" easy	14	—	4·5	1·5
" common, hard	12·5	—	6	1·5
" easy	11·5	—	6·5	2
" easy, for chains	10	5	—	1
For steel	18-19	2-3	1	—
Brass, gun-metal, bronze	1	1	—	—
	1	—	8	8
German silver, gun-metal, bronze	3	—	2	4
	5	6	—	2
Brass, small articles	2	—	5	3
Jewellers', instrument makers', very tough and fluid	11	—	13	—

Coin silver, rolled out thin, is an excellent solder for iron, copper, and very difficultly fusible brass.

Brass, bronze or copper to which 4 to 10 p.c. of silver has been added, forms a solder for thin sheets of mild steel (*Diegel*, Chem. Zeit. 1909, 33, 427).

A very full discussion of hard solders for brass is given by Schwirkus (*Dingl. poly. J.* 293, 64, 89), who recommends copper-zinc-silver alloys containing 40-50 p.c. of copper and 4-12 p.c. silver. For general use and repairs, an alloy of

copper 43, zinc 48, silver 9 parts is best ; for first soldering, copper 48, zinc 48, silver 4 parts should be used.

Copper-zinc-tin solders.—Ordinary brazing processes are carried out with *spelter solder*, a mixture of equal parts of copper and zinc. It may be used on *brass, copper, iron* or *steel*. For pale brass, the proportion of zinc in the solder is increased, while for ironwork that has to be hammered afterwards the proportion of copper should be increased. The composition of a number of brazing solders is given in the following table :—

Remarks on use	Parts of copper	Parts of zinc	Parts of tin
Soft spelter for brass	1	1	—
" " "	4	3	—
Hard " gunmetal, ironwork	2	1	—
" " copper	3	1	—
" " "	7	3	2
Soft " " and brass	4	3	1
Hard " brass (white or button solder)	6·5	1	7·5

Ferrofix brazing process.—This process for brazing broken iron parts, especially *cast iron*, was invented by Pich ; the brass that cements the two pieces together is made to alloy with the iron surfaces as deep as $\frac{1}{16}$ inch. The *flux* used is a mixture of equal parts of sodium carbonate and boric acid, with a little sodium chloride. The *brazing liquid* is prepared by boiling cuprous oxide with concentrated borax solution and allowing the mass to cool down to a sort of paste. The method of procedure is to set the casting to be brazed on firebrick, in perfect alignment ; mix fluxing powder with the brazing liquid and apply to the surfaces with a brush ; heat, and apply more flux until it runs through the joint. Then apply ordinary spelter with a little flux until it flows through thoroughly. Remove the source of heat and continue adding spelter to the joint until the heat of the casting is insufficient to melt it (U.S. Pats. 688030, 647632).

The spelter must not melt below 650° ; hence hard brass must be used. The cuprous oxide of the brazing liquid transfers its oxygen to the carbon contained in the surface layers of the iron, which become decarbonised, while finely divided copper remains diffused through the joint. The hard solder quickly alloys with the copper and the new alloy immediately combines with the red-hot decarbonised soldering surfaces of the cast iron.

Solders for platinum.—Fine gold, laminated and cut into shreds, is employed for soldering platinum. Pure silver may be used also and the following alloys have been proposed : (1) platinum 12, gold 7, silver 1 part ; (2) platinum 1, gold 2, silver 1 part. Platinum joints are usually welded.

Solder for small steel springs.—18 carat gold may be used for repairing small, freshly broken springs ; the spring must then be hardened and tempered.

Solder for German silver.—An alloy of German silver 5, zinc 4 parts, may be used ; *v. also Silver solders (v. supra)*.

Solders for aluminium bronze.—(1) Tin 900, copper 100, bismuth 2 to 3 parts ; silver chloride is used for flux ; (2) gold 89, silver 4·5, copper

6.5 parts; (3) gold 54.5, silver 27, copper 18.5 parts; (4) the zinc-aluminium alloys given for aluminium (*v. infra*).

Soft solders. These contain tin, lead, and sometimes bismuth; for their melting-points, *v. p.* 275. The following table gives the composition of a number of solders, with remarks on their use.

SOFT SOLDERS.

Remarks on use	Parts of tin	Parts of lead	Parts of bismuth	Parts of zinc
Ordinary soft, plumbers', tinmen's	1	1	—	—
Plumbers', coarse	1	3	—	—
„ fine, for lead, zinc, tin, electrotype plates	1	2	—	—
Tinmen's, coarse	3	2	—	—
„ fine	2	1	—	—
„ rough, jobbing work	4	3	—	—
„ blowpipe work	4	2	1	—
Solder for tinned iron	1	7	—	—
„ „ can tops	16	10	1	—
„ „ iron in stone	—	2	—	1
Pewterers', usual	1	1	2	—
„ soft	3	4	2	—
„ „	3	4	1	—
„ „	2	1	1	—
„ „	1	4	2	—
„ rough work	2	1	1	—

Soft solders should be kept carefully free from zinc (*v. J. Soc. Chem. Ind.* 1909, 28, 1139). According to Sperry (*Eng. and Min. J.* 1909, 87, 1140) the addition of *cadmium* to soft solder makes it stronger and more fusible; an alloy of tin 2, lead 1, cadmium 1 part melts at 144.5° and can be used on lead, pewter, Britannia metal, &c.

Chemical solder.—Tin-foil, cut to the size of the joint to be made, is painted over with a solution of sal-ammoniac, then placed between the two portions to be soldered together, and heated upon hot iron, or over a spirit lamp, until the solder melts, the pieces being held together by the hand during the operation. On cooling, a firm joint is the result. This method is very useful for the soldering of small articles together without a soldering iron—*e.g.* pieces of brass or copper wire, the ends of which should first be filed flat.

Solder for aluminium.—No really good solder for aluminium is known, although considerably over fifty alloys have been proposed. The difficulty, which was known to Deville, arises from two causes, (1) the ease with which a film of oxide forms on the surface and the difficulty of properly removing it, and (2) the highly electropositive nature of aluminium, which causes electrolytic action to be set up, particularly if the soldered joint be wetted, and inevitably leads to disintegration at the joint. Ordinary soft solder will not do, but either pure tin or zinc may be used as solder. The zinc joint is very brittle, however, and the tin joint disintegrates since it slowly absorbs oxygen from the air. Aluminium-zinc alloys containing respectively 8, 12, 15, and 20 p.c. of aluminium, may be used (Tissier Bros.), the flux consisting of copaiba balsam 3, Venice turpentine 1 part, and a few drops of lemon juice.

For heavy work, aluminium 12, zinc 80, copper 8 parts may be used; for light work, aluminium 6, zinc 90, copper 4 parts (Dagger, *J. Soc. Chem. Ind.* 1891, 10, 436). Mourey's solder, for blow-pipe work, contains tin 6, zinc 3, aluminium 2, copper 1, silver 1 part. Frishmuth recommends tin 95, bismuth 5 parts, or tin 97, bismuth 3 parts as good soft solders.

The most satisfactory solders for aluminium are zinc-tin alloys, such as the following: (1) Zinc, 15.5; tin, 85.5. (2) Zinc, 8.15; aluminium, 15.5; tin, 76.35. These are applied without flux after tinning the aluminium; the higher the temperature of the latter operation the better the adhesion (U.S. Bureau of Standards, through Amer. Drugg. January, 1924, 23; *Pharm. J.* 1924, 112, 359).

Richard's solder (*J. Soc. Chem. Ind.* 1896, 15, 200; *cf. ibid.* 1899, 18, 281) is largely used; it contains aluminium 1, zinc 11, tin 29, 10 p.c. phosphor-tin 1 part. No flux is required, the solder being self-fluxing owing to the phosphorus it contains. For numerous other solders, *v. J. Soc. Chem. Ind.* from 1892 onwards. It appears preferable to weld or rivet aluminium joints, rather than to solder them.

Cold soldering.—This process may be adopted when the article to be soldered cannot be heated. The *flux* consists of sodium amalgam (1 part of sodium to 50 or 60 of mercury). The *solder* is a copper amalgam prepared as follows: copper is precipitated from a solution of its sulphate by means of zinc, and the spongy metal is washed, drained and shaken with twice its weight of mercury and a little dilute sulphuric acid. The pasty amalgam is quickly formed into small pellets; in a few hours they set to intensely hard lumps. The process consists in heating a pellet until mercury oozes from its surface in small beads, wiping these off and rubbing the pellet into a soft paste in a mortar. The surfaces to be united are amalgamated with the flux, the pasty, prepared pellet then applied and the surfaces pressed tightly together. A perfectly hard joint is obtained in about three hours.

Autogenous soldering.—In this process, soldering takes place by the fusion of the two edges of metal themselves without the interposition of a metallic alloy as a go-between; the metal acts as its own solder. Joints thus made are less liable to rupture when submitted to varying temperatures, &c., than when the common soldering process is employed; moreover, corrosion of the joint owing to electrolytic action does not occur. The process is adopted for the manufacture of sulphuric acid chambers and concentration pans, and the soldering is effected by directing a jet of burning hydrogen or coal-gas upon the edges to be joined together. Brass may be similarly soldered. For copper, iron, steel, platinum, and aluminium, the oxy-hydrogen or oxy-acetylene flame is necessary. Care must be taken to allow no excess of oxygen in the flame; with platinum, however, excess of hydrogen must be avoided, as it is absorbed by the molten metal.

C. H. Meyers (*J. Amer. Chem. Soc.* 45, pp. 2135–2136, September, 1923) describes the procedure to give a satisfactory soldered joint (using tin or a solder of low melting-point) between glass and metal without platinising the glass. Both glass and metal must be very

clean. The glass is cleaned with chromic acid rinsed with distilled water and dried. The metal part is coated with tin or solder and the surface of the molten tin cleaned with zinc chloride. The metal part is allowed to cool, is washed thoroughly with distilled water, and, if necessary, is scrubbed with absorbent cotton free from grease or dirt, and dried. The two parts are then held together above a flame, and as soon as the tin melts, the glass is inserted into the metal without the addition of any flux. One such joint, about 5 mm. diameter, has withstood a pressure of from 60 to 70 atmospheres for three years (Sci. Abstr. 1924, 27, 135).

For some properties of soft-soldered joints, see T. B. Crow (J. Soc. Chem. Ind. 1924, 43, 65, T). For a metal-to-glass joint, see H. N. Ridyard (Sci. Abstr. 1924, 27, 470; from J. Amer. Chem. Soc. 46, 287, February, 1924). For vacuum sealing with Wood's metal, see Welo (Optical Soc. of America, J. and Rev. Sci. Inst. 1924, 8, 453; Sci. Abstr. 1924, 27, 579).

SOLDONA. Trade name for a milk preservative containing formaldehyde and hydrogen peroxide.

SOLENITE *v.* EXPLOSIVES.

SOLIDE JAUNE *v.* AZO-COLOURING MATTERS.

SOLUBILITY. The term 'solubility' denotes the extent to which different substances, in whatever state of aggregation, are miscible with each other. That constituent of the resulting solution which is present in large excess is commonly known as the 'solvent,' the other constituent being the 'solute.' This, however, is merely a convenient distinction, not an essential one, and in cases where it cannot be easily drawn, the term 'miscibility' may be used as synonymous with 'solubility.'

It is proposed to give in this article an outline (1) of the methods available for the determination of solubility or miscibility, (2) of the general results obtained and their significance. For this purpose it is convenient to arrange the material according to the state of aggregation of the substances involved.

Solubility of gases.—Two gases are miscible with each other in all proportions, that is, no definite value can be assigned for the solubility of one gas in another.

The solubility of gases in liquids is a subject to which much attention has been devoted. The extent to which a given gas will dissolve in a given liquid is a function of the temperature and pressure. At any given temperature, the weight of the gas dissolved by a definite volume of the liquid is directly proportional to the pressure. This law was first formulated by Henry (Phil. Trans. 1803, 93, 29, 274), and its general validity has been confirmed by subsequent investigators (for example, Bunsen, Annalen, 1855, 93, 1; Khanikof and Louguine, Ann. Chim. Phys. 1867, 11, 412; Woukloff, Compt. rend. 1889, 108, 674; 109, 61). Strict conformity to the law, however, is exhibited only by those gases which dissolve in the liquid to a comparatively small extent. If the gas is highly soluble—for instance, ammonia or hydrogen chloride in water—then the weight dissolved is no longer proportional to the pressure. An important extension of Henry's law was made by Dalton (Mem. Lit. Phil. Soc. Manchester,

1805, 1, 273), who showed that when a mixture of two different gases is absorbed by a liquid each dissolves proportionally to its partial pressure.

The extent to which a gas is absorbed by a liquid is expressed by the 'absorption coefficient,' or, simply, by the 'solubility.' The absorption coefficient is defined as that volume of the gas (reduced to normal temperature and pressure) which is absorbed by unit volume of the liquid under normal pressure. Thus, if experiment shows that at $t^{\circ}\text{C.}$ and p mm. pressure v cub. cm. of the gas are absorbed by V cub. cm. of the

liquid, then the absorption coefficient $\beta = \frac{v}{V(1+at)}$.

The solubility λ of a gas in a liquid, on the other hand, is defined simply as the volume of the gas absorbed by unit volume of the liquid; so that

$\lambda = \frac{v}{V}$. In the following table are recorded the

absorption coefficients for various common gases in water at different temperatures:—

Temp.	Oxygen	Hydrogen	Nitrogen	Carbon dioxide
0°	0.0492	0.0215	0.0237	1.713
5°	0.0434	0.0204	0.0211	1.424
10°	0.0385	0.0195	0.0191	1.194
15°	0.0346	0.0188	0.0173	1.019
20°	0.0314	0.0182	0.0159	0.878
25°	0.0286	0.0175	0.0147	0.759

The actual determination of the solubility of a gas in a liquid may be carried out in various ways. The method most commonly employed is to bring together known volumes of the gas and the gas-free liquid, to agitate them until saturation has been attained, and then to determine the diminished volume of the gas. Many forms of apparatus, based on this principle, have been suggested from time to time (Bunsen, Annalen, 1855, 93, 1; Mackenzie, Ann. Physik, 1877, 1, 438; Müller, *ibid.* 1889, 37, 24; Timoféeff, Zeitsch. physikal. Chem. 1890, 6, 141; Winkler, Ber. 1891, 24, 89; Setchenow, Ann. Chim. Phys. 1892, 25, 226; Steiner, Ann. Physik, 1894, 52, 275; Gordon, Zeitsch. physikal. Chem. 1895, 18, 1; Roth, *ibid.* 1897, 24, 114; Estreicher, *ibid.* 1899, 31, 176; Braun, *ibid.* 1900, 33, 721; Just, *ibid.* 1901, 37, 342; Skirrow, *ibid.* 1902, 41, 139; Knopp, *ibid.* 1904, 48, 97; Geffcken, *ibid.* 1904, 49, 257; Christoff, *ibid.* 1906, 55, 622; Usher, Chem. Soc. Trans. 1910, 97, 66; Drucker and Moles, Zeitsch. physikal. Chem. 1910, 75, 405). An alternative method is to saturate the liquid and then measure the volume of gas which is expelled on exhausting and boiling out (Hüfner, Ann. Physik, 1877, 1, 632; Dittmar, 'Challenger' Report, Physics and Chemistry, 1, 161; Pettersson and Sondén, Ber. 1889, 22, 1439; Bohr and Bock, Ann. Physik, 1891, 44, 318). Instead of expelling and measuring the gas present in the saturated liquid, it may be determined chemically if a suitable method is available (Schönfeld, Annalen, 1855, 95, 1; Carius, *ibid.* 1856, 99, 129; Roscoe and Dittmar, Chem. Soc. Trans. 1860, 12, 128; Sims, *ibid.* 1862, 14, 1; Watts, Annalen Suppl. 1865, 3, 227; Winkler, Ber. 1889, 22, 1764; Bohr, Ann. Physik, 1900, 1, 244; Fox, Zeitsch. physikal. Chem. 1902, 41, 458; Clowes and Biggs, J. Soc. Chem. Ind. 1904, 23, 358). In certain cases an aspiration

method of finding the partial pressure of a gas in its solutions may be utilised in the determination of solubility coefficients (Gaus, *Zeitsch. anorg. Chem.* 1900, 25, 236; Abegg and Riesenfeld, *Zeitsch. physikal. Chem.* 1902, 40, 84; McLauchlan, *ibid.* 1903, 44, 600; Jones, *Chem. Soc. Trans.* 1911, 99, 392; Dobson and Masson, *ibid.* 1924, 125, 668; Dunn and Rideal, *ibid.* 676).

As a general rule, the solubility of a gas in a liquid diminishes as the temperature rises, and a connection has been traced between this diminution and the viscosity of the liquid. It appears that the diminution in the absorption coefficient for any temperature interval is approximately proportional to the corresponding diminution in the viscosity coefficient of the solvent (Winkler, *Zeitsch. physikal. Chem.* 1892, 9, 171; Thorpe and Rodger, *Chem. Soc. Trans.* 1894, 65, 782). Cases, however, are known in which the solubility of a gas increases as the temperature rises. Thus, the existence of a minimum solubility at 60° has been shown for hydrogen in water (Bohr and Bock, *Ann. Physik*, 1891, 44, 318) and for the rare gases in water (Estreicher, *Zeitsch. physikal. Chem.* 1899, 31, 176; von Antropoff, *Proc. Roy. Soc. A*, 1910, 83, 474). Further, Just (*Zeitsch. physikal. Chem.* 1901, 37, 342) has found that the solubilities of nitrogen, hydrogen, and carbon monoxide in a number of organic solvents are greater at 25° than at 20°. In this connection attention may be directed to the work of Sieverts (*Zeitsch. physikal. Chem.* 1910, 74, 277; 1911, 77, 591), who found that the solubilities of hydrogen and sulphur dioxide in molten copper increase with rising temperature.

The factors which determine the solubility of a gas in a pure liquid are not clearly understood, but it is at least highly probable that, *ceteris paribus*, the greater the compressibility of the solvent and the smaller the volume change associated with the absorption of the gas, the greater is the solubility (see Ritzel, *Zeitsch. physikal. Chem.* 1907, 60, 319). In this connection, it should be pointed out that the relative volume change in a liquid resulting from absorption of a gas is proportional to the concentration of the gas (Ångström, *Ann. Physik*, 1882, 15, 297; 1888, 33, 223; Mackenzie and Nichols, *ibid.* 1878, 3, 134; Nichols and Wheeler, *Phil. Mag.* 1881, 11, 113; Ritzel, *l.c.*). Further, the study of the solubility of gases in mixed organic solvents has revealed the existence of points of maximum solubility, such points corresponding with the occurrence of minimum surface tension (Skirrow, *Zeitsch. physikal. Chem.* 1902, 41, 139; compare Christoff, *ibid.* 1906, 55, 622).

Much attention has been devoted to the influence of salts and other dissolved substances on the absorption of gases by water. Provided there is no chemical action between the gas and the other dissolved substance, it is generally the case that the gas is less soluble in the solution than in pure water at the same temperature (see, for example, Steiner, *Ann. Physik*, 1894, 52, 275; Gordon, *Zeitsch. physikal. Chem.* 1895, 18, 1; Roth, *ibid.* 1897, 24, 114; Braun, *ibid.* 1900, 33, 721; Knopp, *ibid.* 1904, 48, 97; Geffcken, *ibid.* 1904, 49, 257; Usher, *Chem. Soc. Trans.* 1910, 97, 66). An important result deducible from these and other investigations is

that when a number of salts are arranged according to their power of lowering the solubility of one gas in water, the order is very nearly the same as when they are arranged with reference to their influence on the solubility of another gas. It appears, therefore, that the diminished solvent power of a salt solution as compared with pure water is mainly determined, not by the specific nature of the dissolved gas, but by some factor involved in the relationship of the water and the salt. What this factor is, has not yet been determined with certainty. It has been suggested that the influence exerted by salts is a function of the internal pressure or the compressibility of the solution (Euler, *Zeitsch. physikal. Chem.* 1899, 31, 368; Geffcken, *ibid.* 1904, 49, 257; Ritzel, *ibid.* 1907, 60, 319). On the other hand, interaction between the molecules or ions of the dissolved substances has been assumed to account for the influence of salts in lowering solubility (Levin, *Zeitsch. physikal. Chem.* 1906, 55, 503; Rothmund, *ibid.* 1909, 69, 523). Again, it has been suggested that the lower solvent power of a salt solution as compared with water is connected with the hydration of the salt (Rothmund, *Zeitsch. physikal. Chem.* 1900, 33, 413; Baur, *Ahrens' Sammlung*, 1903, 8, 466; Lowry, *Trans. Faraday Soc.* 1905, 1, 197; Philip, *Chem. Soc. Trans.* 1907, 91, 711; Hudson, *Zeitsch. Elektrochem.* 1908, 14, 821).

The solubility of *gases in solids* is a more complex phenomenon than the solubility of gases in liquids, for while in the latter case the equilibrium concentration of the gas in the condensed phase may be taken as uniform throughout, it is frequently necessary for the system gas+solid (chemical combination between the two being excluded from consideration) to assign a special significance to the *surface* of the solid as distinct from its interior mass. If a gas at some definite pressure is put in contact with a gas-free porous solid, such as charcoal, there is an extraordinarily rapid fall of pressure in the first short period, followed by a further slow diminution. These two stages in the pressure fall are associated with the surface layer and the interior portion of the solid respectively, and the term 'adsorption' is now commonly employed to describe the taking up of a gas specially by the surface of a solid, while 'absorption' refers more particularly to the slow penetration or solution of the gas in the body of the solid. McBain, who has shown how these two stages may be differentiated in the system charcoal+hydrogen (*Phil. Mag.* 1909, 18, 916), has proposed the term 'sorption' to cover the taking up of a gas by a solid as a whole, *i.e.* to include both 'adsorption' and 'absorption.'

The quantity of gas taken up by a solid under varying pressure increases more slowly than the pressure—a relation which, for constant temperature, may be expressed generally

by a formula of the type $c_s = k \cdot p^{\frac{1}{n}}$, where c_s is the quantity of gas held by one gram of the solid at equilibrium, p is the pressure, n is a number greater than unity, and k is a constant (see, for example, Travers' study of the isotherms for carbon dioxide+carbon, *Proc. Roy. Soc. A*, 1906, 78, 9; Richardson's investi-

gation of the adsorption of carbon dioxide and ammonia by charcoal, J. Amer. Chem. Soc. 1917, 39, 1828).

In the case of vapours (*e.g.* water and alcohol) adsorbed by charcoal the isotherms at higher pressures may turn and become convex to the pressure axis, this feature being connected probably with the condensation of the substance in the pores of the charcoal (Gustaver, Koll. Chem. Beihefte, 1922, 15, 185). The same factor is probably operative at higher pressures in the adsorption of nitrogen and hydrogen by charcoal and silica at liquid air temperatures (Briggs, Proc. Roy. Soc. A, 1921, 100, 88).

The forces by which the adsorbed gas is attached to the solid surface have been the subject of much discussion, and are regarded by some investigators as purely physical, by others as essentially chemical, in character (*see*, for example, Langmuir, J. Amer. Chem. Soc. 1916, 38, 2221; 1917, 39, 1848; 1918, 40, 1361; Williams, Proc. Roy. Soc. A, 1919, 96, 287, 298).

In view of the significance of the surface in the sorption of gases by solids, it will be clear that the quantity of a gas taken up by unit weight of the solid at a given temperature and pressure is not a constant, but varies with the surface development. Much of the research carried out in 1915-8 on the defensive side of gas warfare aimed at the production of a charcoal of maximum efficiency, this efficiency standing in a very close relationship to the extent and condition of the surface. It is possible by heat treatment alone, or by heating in steam, to 'activate' a charcoal to a surprising degree (*cf.* Lemon, Physical Review, 1919, 14, 281; Sheldon, *ibid.* 1920, 15, 135), and this possibility is not confined to those charcoals (*e.g.* animal charcoal and cocoanut-shell charcoal) which were previously supposed to exhibit sorption to an exceptional extent. The activation resulting from heat treatment has been the subject of repeated investigation, and it has been generally connected either with the progressive removal of hydrocarbons from the surface of the charcoal (Lamb, Wilson and Chaney, J. Ind. Eng. Chem. 1919, 11, 420; Sheldon, *l.c.* and Physical Review, 1920, 16, 165), or with the partial oxidation of the charcoal (Philip, Dunnill and Workman, Chem. Soc. Trans. 1920, 117, 362; *cf.* Bartell and Miller, J. Amer. Chem. Soc. 1922, 44, 1866). In any case, the activation is found to be accompanied by an increase in porosity and a decrease in apparent or bulk density.

The extent to which gases are taken up by charcoal increases very notably as the temperature is lowered, and on this fact is based the application of cooled charcoal in the production of high vacua, a method first employed by Dewar. The following figures will serve to illustrate the significance of temperature in this connection:—

		Volume of gas sorbed by 1 gram charcoal	
		at 0°C.	at -185°C.
Hydrogen	.	4 cub. cm.	139 cub. cm.
Nitrogen	.	15 „	155 „
Oxygen	.	18 „	230 „

Other phenomena which may be considered from the standpoint of gas sorption are the

retention of moisture by glass surfaces, the variation in the moisture content of textile fabrics with the humidity of the atmosphere, and the occlusion of gases by metals. Under the last category much interest attaches to the case of hydrogen+palladium, the earlier work on which has been summarised by Holt, Edgar and Firth (Zeitsch. physikal. Chem. 1913, 82, 513; *see also* article on PALLADIUM). Later work (Andrew and Holt, Proc. Roy. Soc. A, 1913, 89, 170; Holt, *ibid.* 1914, 90, 226; Sieverts, Zeitsch. physikal. Chem. 1914, 88, 105; Firth, Chem. Soc. Trans. 1920, 117, 171; 1921, 119, 1120) indicates that the activity of palladium in the sorption of hydrogen depends on the presence of an amorphous variety of the metal, and that the phenomenon is predominantly one of adsorption at low temperatures and of absorption at high temperatures.

The power of metals (palladium and platinum) to take up hydrogen to a greater or less extent has an obvious bearing on the permeability of these metals, and the study of this question by various workers (Ramsay, Phil. Mag. 1894, 38, 206; Winkelmann, Ann. Physik, 1901, 6, 104; 1902, 8, 338; 1905, 16, 773; 1905, 17, 589; Schmidt, *ibid.* 1904, 13, 747; Richardson, Nicol and Parnell, Phil. Mag. 1904, 8, 1) has led to the adoption in some quarters of the view that when hydrogen dissolves in a metal it does so in the atomic form. It appears that hydrogen desorbed from palladium is somewhat more active than the gas in the ordinary molecular condition (Anderson, Chem. Soc. Trans. 1922, 1153).

From the technical standpoint also the occlusion of gases by metals is of interest in connection with the influence of blowholes in a casting on the physical properties of the metal (*see* Trans. Faraday Soc. 1919, 14, 173).

Solubility of liquids in liquids.—As regards their mutual solubility, a pair of liquids is commonly assigned to one of three classes. They may be miscible in all proportions, they may be only partially miscible, or they may be practically immiscible. Such a classification, however, has only a general value, for the difference between the second and third classes is merely one of degree, and the line of division between the first and second classes is displaced by altering the temperature.

In finding the solubility of one liquid in another when the solubility is very small, as, for instance, in the case of chloroform or carbon disulphide in water, two methods may be adopted. One consists in bringing together a large known volume of the first liquid with a small known volume of the second, shaking until saturation has been reached, and then finding the volume of the second liquid remaining undissolved (Schuncke, Zeitsch. physikal. Chem. 1894, 14, 331; Bödtker, *ibid.* 1897, 22, 511; Herz, Ber. 1898, 31, 2669; Rex, Zeitsch. physikal. Chem. 1906, 55, 355). Another method is to shake quantities of the two liquids together until they are mutually saturated, and then remove portions of each layer for analysis (Chancel and Parmentier, Compt. rend. 1884, 99, 892; 1885, 100, 773; Walker, Zeitsch. physikal. Chem. 1890, 5, 196; Klobbie, *ibid.* 1897, 24, 616; Euler, *ibid.* 1899, 31, 364; Osaka, Mem. Coll. Sci. Eng. Kyoto, 1909-1910,

2, 21). Determinations are naturally made at various temperatures.

In the case of liquids the mutual solubility of which is greater than in the afore-mentioned cases, the method commonly employed is a synthetic one. That is, weighed quantities of the two liquids are put in a tube, which is then sealed and suspended in a bath of water or other suitable liquid. The temperature of the bath is altered until the contents of the tube become uniform and determinations of this point are then repeatedly alternated with determinations of the temperature at which, as indicated by the appearance of turbidity, the uniform contents of the tube begin to separate into two layers (Guthrie, *Phil. Mag.* 1884, 18, 22, 495; Alexéeff, *Ann. Physik.* 1886, 28, 305; Rothmund, *Zeitsch. physikal. Chem.* 1898, 26, 433; Bingham, *Amer. Chem. J.* 1907, 37, 549; 38, 91; Flaschner and MacEwen, *Chem. Soc. Trans.* 1908, 93, 1000). Experience shows that these two points, the one observed with rising, the other with falling temperature, are generally very close together, and the mean of the observed temperatures may be taken as the point at which the liquid is saturated.

For each temperature there are generally found two saturated mixtures of different composition, corresponding to the two layers obtained when the pure liquids are shaken up together. As a rule, the mutual solubility of two liquids increases as the temperature rises, and the compositions of the conjugate layers approximate more and more to each other. In such a case (Fig. 1), the two solubility curves, *i.e.* the

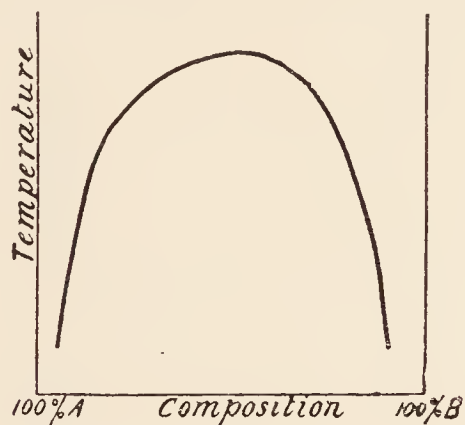


FIG. 1.

curve representing the solubility of B in A and that representing the solubility of A in B, join at a point above which the liquids are completely miscible. As suggested by Masson (*Zeitsch. physikal. Chem.* 1891, 7, 500), who emphasises the parallelism between the case just described and the gradual approximation in density of a liquid and its saturated vapour, the temperature above which two partially miscible liquids become miscible in all proportions is called the 'critical solution temperature.' The existence of this temperature limit has been recorded for such cases as phenol and water, aniline and water, benzoic acid and water, carbon disulphide and methyl alcohol, methylethylketone and water. In these and other instances, it is further found that the middle points of the horizontal chords cut off between the two branches of the solubility curve lie on a straight line—another analogy with the density-temperature curve for a pure liquid and its saturated vapour (*see* Rothmund, *l.c.*). It is noteworthy

that bismuth+zinc and lead+zinc furnish examples of limited miscibility in the fused state: the solubility curve for each pair is of the foregoing type (Spring and Romanoff, *Zeitsch. anorg. Chem.* 1897, 13, 29).

In a few cases—for instance, triethylamine and water, β -collidine and water, 1-methylpiperidine and water—the change of miscibility with temperature is the opposite of that described above. The mutual solubility increases as the temperature falls and there is a limit, known as the 'lower critical solution temperature,' below which the liquids are miscible in all proportions, and above which separation into two layers takes place increasingly as the temperature

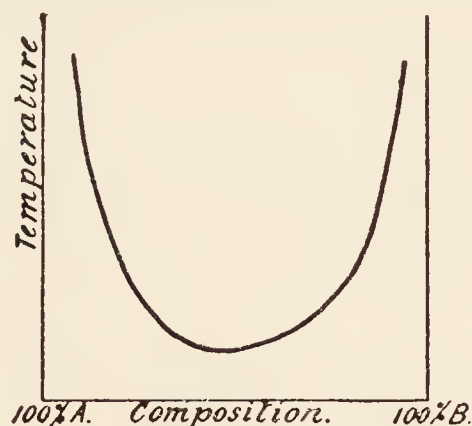


FIG. 2.

rises. The relation between solubility and temperature in such a case is represented in Fig. 2.

For nicotine and water (Hudson, *Zeitsch. physikal. Chem.* 1904, 47, 113), and 2-methylpiperidine and water (Flaschner and MacEwen, *Chem. Soc. Trans.* 1908, 93, 1000; *cf.* MacEwen, *ibid.* 1923, 123, 2286), both upper and lower critical solution temperatures are known, and the complete solubility curve is a closed ring. According to Rothmund (*l.c.*), this is the normal type of solubility curve for a pair of partially miscible liquids. There need not, however, be an upper critical solution temperature in every such case (Kuenen and Robson, *Zeitsch. physikal. Chem.* 1899, 28, 342), and the occurrence of a lower critical solution temperature has been held to be abnormal (Dolgolenko, *ibid.* 1908, 62, 499).

The influence of high pressures on the mutual solubility of liquids has been investigated by Kohnstamm and Timmermans (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, 15, 1021; *Arch. Néerland*, 1922, 6, 147).

The mutual solubility of two liquids may be materially modified by the addition of a third substance. In this way two liquids which are miscible in all proportions may be made to undergo at least partial separation: for example, a homogeneous mixture of propyl alcohol and water, which are miscible in all proportions at ordinary temperatures, separates into two layers on the addition of salt. In the case of two liquids which are only partially miscible, the area of non-miscibility may be notably extended or reduced by the introduction of a third substance, and a measure of this influence is found in the effect of the third substance on the critical solution temperature. According to Timmermans (*Zeitsch. physikal. Chem.* 1907, 58, 129), who has made an exhaustive study of this phenomenon, the upper critical solution temperature is lowered when the solubilities of the third

substance in the two liquids are of the same order of magnitude. If the third substance is much more soluble in the one liquid than in the other the critical solution temperature is raised, *i.e.* the area of non-miscibility is extended. It is noteworthy that when different salts are arranged according to their ability to cause the system water+propyl alcohol to separate into two phases, or according to their power to raise the critical solution temperature of the system water+phenol, the order is approximately the same as when they are arranged according to the magnitude of their influence on the solubility of gases in water. These effects have an obvious bearing on the well-known practice of 'salting out' organic compounds from their aqueous solutions (*cf.* Thorin, *Zeitsch. physikal. Chem.* 1915, 89, 685).

Solubility of solids in liquids.—The equilibrium between a solid and a liquid is established more slowly than that between two liquids, and this fact explains the precautions that must be taken if the solubility of a solid in a liquid is to be determined with rapidity and yet with accuracy. The solvent and the finely-divided solid are put in a suitable glass vessel and shaken together at constant temperature, either intermittently by hand, or regularly by some mechanical arrangement. This is continued until the solution is saturated, when samples are withdrawn and analysed. The time necessary for the attainment of saturation varies from one case to another, and should be ascertained by preliminary experiments in which samples of the solution are taken out at intervals until the quantity of substance in solution is found constant. A guarantee that the value so found for the solubility is the correct one at the temperature of observation may be obtained by approaching the saturation point from the other side. A saturated solution is prepared at a higher temperature (on the supposition that the solubility increases with rising temperature), and is then put in a bath at the desired temperature, when the excess of solid in solution gradually separates out, the attainment of equilibrium being preferably facilitated by shaking or stirring. The analysis of the saturated solution obtained in this way ought to give the same result as the previous method (*see* Andreae, *J. pr. Chem.* 1884, 29, 456).

In withdrawing samples of the saturated solution an ordinary pipette may be used, with an auxiliary tube containing a plug of glass wool or cotton wool to keep back the solid. If the temperature at which the solution has been saturated is higher than the temperature of the room, the pipette may have to be warmed slightly to avoid crystallisation of the solid. It is, however, preferable in such cases to carry out the operation of filtration into a weighed vessel inside the constant temperature bath.

Many forms of apparatus for carrying out these various operations have been described (*see*, for instance, V. Meyer, *Ber.* 1875, 8, 998; Andreae, *l.c.*; Carnelley and Thomson, *Chem. Soc. Trans.* 1888, 53, 782; Meyerhoffer, *Zeitsch. physikal. Chem.* 1890, 5, 99; Reicher and van Deventer, *ibid.* 1890, 5, 560; Nicol, *Phil. Mag.* 1891, 31, 374; Noyes, *Zeitsch. physikal. Chem.* 1892, 9, 606; Arrhenius, *ibid.* 1893, 11, 392; Goldschmidt, *ibid.* 1895, 17, 152; Pawlewski,

Ber. 1899, 32, 1040; Lumsden, *Chem. Soc. Trans.* 1902, 81, 350). For higher temperatures, such as the boiling-point of the solvent and beyond it, the solubility apparatus must be specially modified (*see* V. Meyer, *Ber.* 1875, 8, 1000; Tilden and Shenstone, *Phil. Trans.* 1884, 175, 23; Goeckel, *Chem. Zentr.* 1897, ii. 401; Thiele and Calberla, *Zeitsch. angew. Chem.* 1906, 19, 1263; Schroeder, *Zeitsch. anal. Chem.* 1909, 48, 349; Tyrer, *Chem. Soc. Trans.* 1910, 97, 621; Tschugaev and Chlopin, *Zeitsch. anorg. Chem.* 1914, 86, 154). Attempts have been made to determine solubility by finding the temperature at which a minute quantity of the solid in contact with its solution neither increases nor diminishes in amount (Andreae, *l.c.*; Alexéeff, *Ann. Physik.* 1886, 28, 305; Schroeder, *Zeitsch. physikal. Chem.* 1893, 11, 453).

In the case of very sparingly soluble salts, such as the silver halides in water, the ordinary method of determining solubility is impracticable, because the amount of solid in the saturated solution cannot be estimated with any accuracy. For the silver halides in water, it is true, Whitby (*Zeitsch. anorg. Chem.* 1910, 67, 107) suggests heating the saturated solution with sucrose and sodium hydroxide under standard conditions and estimating colorimetrically the quantity of colloidal silver produced. But various physical methods are available for determining the solubility in water of sparingly soluble salts generally. Thus the electrical conductivity of the saturated solution may be compared with that of pure water, and the solubility of the salt deduced therefrom (Holleman, *Zeitsch. physikal. Chem.* 1893, 12, 125; Kohlrausch and others, *ibid.* 1893, 12, 234; 1904, 50, 355; *Sitzungsber. K. Akad. Wiss. Berlin*, 1901, 1018; Böttger, *Zeitsch. physikal. Chem.* 1903, 46, 521; 1906, 56, 83; Weigel, *ibid.* 1907, 58, 293). A knowledge also of the potential difference between a suitable electrode and the saturated solution of the sparingly soluble salt in question permits a calculation of the solubility (Goodwin, *Zeitsch. physikal. Chem.* 1894, 13, 641; Morgan, *ibid.* 1895, 17, 533; Thiel, *Zeitsch. anorg. Chem.* 1900, 24, 49; Immerwahr, *Zeitsch. Elektrochem.* 1901, 7, 477). Another method has been suggested by Biltz (*Zeitsch. physikal. Chem.* 1907, 58, 288), who shows that in the case of two salts giving a sparingly soluble compound by double decomposition, the ultra-microscope indicates when the solutions have been so far diluted that no precipitate forms. From such an observation the solubility of the precipitate may be calculated.

In the majority of cases, the solubility of a given solid in a given liquid increases as the temperature rises, and as a rule the solubility-temperature curve is convex to the temperature axis. No general law, however, is known which connects solubility and temperature. A decrease of solubility with rising temperature over the whole or part of the temperature range, has been observed in a number of cases, *e.g.* calcium sulphate, calcium hydroxide, sodium sulphate, ferrous sulphate (Tilden and Shenstone, *Phil. Trans.* 1884, 175, 23; Étard, *Compt. rend.* 1888, 106, 206, 740; Lieben and others, *Monatsh.* 1894, 15, 404; Lumsden, *Chem. Soc. Trans.* 1902, 81, 350). In some of these and other

instances, points of maximum and minimum solubility occur on the solubility-temperature curve, *e.g.* for the calcium and barium salts of the fatty acids in water. Maxima are observed also in numerous cases where the dissolved solid forms a compound with the solvent: this occurs most commonly for the combination salt+water (*see*, for example, Roozeboom, *Zeitsch. physikal. Chem.* 1893, 10, 477). Discontinuities occur on the solubility-temperature curve at points where the solid in contact with the solution undergoes a change. Such breaks may be associated with the disappearance of one hydrate of a salt and the appearance of another (*see* de Coppet, *Ann. Chim. Phys.* 1883, 30, 429; Roozeboom, *Zeitsch. physikal. Chem.* 1890, 5, 198; 1893, 10, 477; Donnan and Burt, *Chem. Soc. Trans.* 1903, 83, 335), or with the transition of one crystalline form of a substance into another (Rabe, *Zeitsch. physikal. Chem.* 1901, 38, 175; Müller and Kaufmann, *ibid.* 1903, 42, 497; Steele and Johnson, *Chem. Soc. Trans.* 1904, 85, 113). At temperatures other than those corresponding with the breaks, the more stable form is the less soluble (*see, e.g.* Roozeboom, *Zeitsch. physikal. Chem.* 1893, 10, 477; Rabe, *ibid.* 1901, 38, 175; Philip, *Chem. Soc. Trans.* 1915, 103, 287; Philip and Colborne, *ibid.* 1924, 125, 492).

Although there is no general law permitting the prediction of the relation between solubility and temperature for a given solvent and solute, there is a close connection, deducible thermodynamically, between the heat of solution and the variation of solubility with temperature (Le Chatelier, *Compt. rend.* 1885, 100, 441; van't Hoff, *Kongl. Svenska Vet. Akad. Handl.* 1886, 21, 17). According to this, the solubility of a solid in a liquid must increase with rising temperature when the process of dissolution is accompanied by the absorption of heat, and decrease with rising temperature when there is evolution of heat. The validity of this relationship has been confirmed by experiment (*see* Reicher and van Deventer, *Zeitsch. physikal. Chem.* 1890, 5, 559; van Deventer and van de Stadt, *ibid.* 1892, 9, 43; von Stackelberg, *ibid.* 1898, 26, 533).

For the influence of pressure on solubility, *see* Sill, *J. Amer. Chem. Soc.* 1916, 38, 2632.

As in the case of gases and liquids, the solubility of a solid in a liquid may be profoundly modified by the presence of a third substance. This may be due to definite chemical action; iodine, for instance, is more soluble in potassium iodide solutions than in pure water, and silver chloride, almost insoluble in pure water, dissolves readily in potassium cyanide solution. In other cases, the solubility change appears to be connected with a displacement of equilibrium, as when the solubility of a salt is diminished by adding another electrolyte with a common ion, or when it is increased by adding another electrolyte with both ions different. The influence of salts on the solubility of non-electrolytes is more difficult to explain, the general, although not the universal, rule being that a non-electrolyte is less soluble in a salt solution than in pure water at the same temperature. The solubility of a non-electrolyte in water is sometimes raised, sometimes lowered, by the addition of another non-

electrolyte. (For a detailed discussion of this whole question, *see* Rothmund's *Löslichkeit und Löslichkeitsbeeinflussung*, vol. vii. of Bredig's *Handbuch der angewandten Physikalische Chemie*; also Eyre, *Brit. Assoc. Reports*, 1910, 425; 1912, 795.)

As regards the factors which determine the solubility of a given solid in a given solvent, different views are held. From the mass of data available a number of regularities have been deduced, but these are of limited scope. Thus, for instance, it is known that with water as solvent, the solubility of the monohydric alcohols diminishes as the preponderance of the alkyl radicle increases and that an increase in the number of hydroxyl groups introduced into a molecule leads to an increased solubility. For isomeric substances, certain rules have been deduced, such as that the more fusible isomer is also the more soluble in a given solvent, and that the ratio of the solubilities of two isomers in different solvents is approximately the same. (*See* Lumsden, *Chem. Soc. Trans.* 1902, 81, 363; Rothmund, *l.c.*; Eyre, *l.c.*; Sidgwick and others, *Chem. Soc. Trans.* 1921-1924.)

For expositions of various views of the different factors affecting solubility and miscibility reference may be made to Tyrer, *J. Phys. Chem.* 1912, 98, 69; Peddle and Turner, *Chem. Soc. Trans.* 1913, 1202; Holmes, *ibid.* 1913, 2147; 1915, 1471; 1918, 263; Hildebrand, *J. Amer. Chem. Soc.* 1916, 38, 1452; Harkins and King, *ibid.* 1919, 41, 970; Ephraim, *Ber.* 1921, 54, 379; Brönsted, *Chem. Soc. Trans.* 1921, 574; *J. Amer. Chem. Soc.* 1922, 44, 938.

J. C. P.

SOLUBLE or WATER GLASS.—This is the name given to alkaline silicates which may be prepared by fusing sand with sulphates or carbonates of sodium or potassium, or by heating caustic alkalis in solution with finely divided silica, such as infusorial earth. The products of the fusion have the appearance of glass, but may be dissolved in water to form viscous solutions. The ratio of alkali to silica may vary between ratios 1:1 and 1:4. Glasses containing as much as two molecules of silica for each Na_2O may be dissolved in boiling water. Those containing larger proportions of silica are much more difficult to dissolve, due to the tendency of the alkali to pass into the solution more rapidly than silica, leaving on each particle a gelatinous, insoluble layer. Water glass is commercially known as silicate of soda.

The solution is used for a large variety of purposes. It has valuable detergent properties and is used extensively in laundry soap. It is an essential ingredient in the preparation of fireproof and acidproof cements and lutings, which can be made to set rapidly or slowly in the cold by the addition of more or less active mineral ingredients, which tend to form insoluble silicates. The joints thus formed increase in strength and adhere to the adjacent bricks more strongly as the temperature of sintering is reached.

Silicate of soda is used in the preparation of abrasive wheels and as an adhesive for asbestos, on account of its fireproof properties. Eggs immersed in a 4 p.c. solution of water glass of low alkaline content are cheaply preserved. More recently silicate of soda has come into

extensive use as an adhesive for laminating plies of paper to make a heavy paper board used in building construction for interior partitions, and for heavy paper cases used in the transport of a great variety of commercial wares. It is possible to make with sodium silicate joints having a tensile strength of 500 lbs. per square in., and artificial stone having a tensile strength of 2000 lbs. per square in. V. art. SODIUM.

SOLUPYRINE. Trade name for calcium acetyl salicylate.

SOLUROL. Trade name for nucleotin phosphoric acid (thymeric acid).

SOLUTION. The history of chemistry has been marked by constant speculation on the nature of the system formed when a substance dissolves in a liquid. The theories held at one time or another in regard both to the process of dissolution and to the constitution of solutions may be roughly classed as chemical or physical, according to the nature of the forces supposed to be at work. In either case, however, the experimental basis is furnished mainly by the physical properties of solutions, and the utility and fitness of any theory of solution must be judged by the extent to which it is capable of interpreting these properties.

It is impossible within the limits of this article to deal exhaustively with the physical properties of solutions, but it is proposed to discuss the experimental results which have been achieved in connection with some of the more salient characteristics, and then to sketch the modern theories, based on these properties, which bear on the question of the nature of solution.

Density.—It has been found that when aqueous solutions of different salts of the same molecular concentration (for example, 1 mol. salt to 100 mols. water) are compared, the density of the solution increases with the molecular weight of the dissolved salt. This rule, however, is not strictly valid unless the metals in the salts belong to the same group (*see* Kremers, *Pogg. Ann.* 1854, 92, 497; 1855, 94, 87, 255; Mendeléeff, *Ber.* 1884, 17 (Ref.), 155; Gerlach, *Zeitsch. anal. Chem.* 1888, 27, 271; 1889, 28, 290, 466; Charpy, *Compt. rend.* 1892, 114, 539). More definitely quantitative in character is the observation made by Valson, that if solutions of two salts AB and AB' are compared, each solution containing 1 gram-equivalent in 1 litre of water, the difference in density is practically the same whatever the acid radicle A may be. Similarly, the difference in density of comparable solutions of two salts AB and A'B with a common positive radicle is independent of B. There may, therefore, be assigned to each radicle, positive or negative, a certain figure or 'modulus,' such that the density of a normal solution of any salt can be calculated approximately by simply adding together the two values for the radicles contained in the salt (Valson, *Compt. rend.* 1871, 73, 441). This additive character of the density of dilute aqueous salt solutions has been confirmed by subsequent observers (*see* Ostwald, *J. pr. Chem.* 1878, 18, 353; Nicol, *Phil. Mag.* 1883, 16, 121; 1884, 17, 150; Bender, *Ann. Physik*, 1883, 20, 560). Bender was able to extend Valson's law of moduli on the strength of the observation that if Δ represents the

difference between the densities of two salt solutions, each containing m equivalents of salt per litre of solution, then Δ/m is a constant for the two salts at a given temperature.

Investigation has shown that the density of a salt solution increases less rapidly than the concentration and that, accordingly, the value of the expression $\frac{s-1}{m}$, where s is the density and m is the concentration in gram-equivalents per litre, decreases as the concentration of the solution increases. If $\frac{s-1}{m}$ is plotted against m , the decrease is often found to be exceptionally marked in very dilute solutions, although the curves obtained by plotting $\frac{s-1}{m}$ against $m^{\frac{1}{2}}$ are practically straight lines (Kohlrausch and Hallwachs, *Ann. Physik*, 1893, 50, 118). More recently it has been found that within certain concentration limits the quantity $\frac{s-1}{m}$ is a linear function of the degree of dissociation as defined by Arrhenius (*see* Magie, *Physical Review*, 1907, 25, 171; Heydweiller, *Ann. Physik*, 1909, 30, 873; 1910, 31, 1063; Clausen, *ibid.* 1912, 37, 51; 1914, 44, 1067).

Much attention has been devoted to the character of the density-concentration curves in the case of aqueous solutions of sulphuric acid and ethyl alcohol. When the first or second differential of the sp.gr.— $\frac{ds}{dp}$ or $\frac{d^2s}{dp^2}$ —is plotted against the percentage composition p , a series of straight lines is obtained in place of the continuous curve which results when s is plotted against p . It is maintained by some investigators that the discontinuities thus exhibited correspond with the formation of definite compounds between water and the dissolved substance (*see* Mendeléeff, *Ber.* 1886, 19, 379; *Zeitsch. physikal. Chem.* 1887, 1, 273; *Chem. Soc. Trans.* 1887, 51, 778; Pickering, *ibid.* 1890, 57, 64; compare Crompton, *ibid.* 1888, 53, 116; Arrhenius, *Phil. Mag.* 1889, 28, 30; Pickering and others, *Chem. Soc. Proc.* 1891, 105).

Closely related to the subject of density is the question how far the process of dissolution is accompanied by change of volume. A study of mixtures of organic liquids from this point of view has shown that the differences between the densities directly determined and the values calculated on the assumption that no change of volume occurs on mixing are considerably greater where associated liquids are involved than where both liquids are 'normal.' In the majority of cases where the mixed liquids belong to the latter class the observed density is less than the calculated value (Linebarger, *Amer. Chem. J.* 1896, 18, 429; *cf.* Bramley, *Chem. Soc. Trans.* 1916, 109, 10, 434).

The investigation of solutions of such substances as paraffin, naphthalene, anthracene, dinitrobenzene and benzil in non-associated organic solvents has shown that the volume occupied by the solute in solution is approximately a constant, independent of the concentration and, with certain limitations, of the solvent. This volume, further, is approximately equal to the volume which the pure solute would occupy in the liquid state at the

same temperature (Beilby, Chem. Soc. Trans. 1883, 43, 138; Nicol, *ibid.* 1896, 69, 142; Forch, Ann. Physik, 1905, 17, 1012; Lumsden, Chem. Soc. Trans. 1907, 91, 24; Dawson, *ibid.* 1910, 97, 1041, 1896; Tyrer, *ibid.* 2620).

The changes of volume which accompany the dissolution of a substance in water are much more notable. For some anhydrous salts and other substances, such as sodium hydroxide in dilute solution, the volume of the solution is actually less than the volume occupied by the pure solvent (*see* Macgregor, Chem. News, 1887, 55, 3). Attempts to find the volume occupied by a solute in aqueous solution are generally based on the assumption that the volume of the solvent in the solution is the same as if it were in the pure state. On this basis the molecular solution volume v_m , that is, the volume occupied by 1 gram-molecule of the dissolved substance,

is given by the formula $v_m = \frac{m+w}{d} - \frac{w}{\delta}$, where m

is the molecular weight of the solute in grams, w is the weight of water in which the gram-molecule is dissolved, d and δ are the densities of solution and pure water respectively (*see* Nicol, Phil. Mag. 1883, 16, 121; 1884, 18, 179; Kohlrausch and Hallwachs, Ann. Physik, 1893, 50, 118; 1894, 53, 14; Kohlrausch, *ibid.* 1895, 56, 185; Traube, Ueber den Raum der Atome, Ahrens' Sammlung, 1899, 4, 255). The value of the molecular solution volume for a non-electrolyte in aqueous solution does not vary much, as a rule, with the concentration (*see* also Wanklyn, Chem. News, 1892, 65, 122). For an electrolyte, on the other hand, the molecular solution volume diminishes as the concentration of the solute diminishes and, in many cases at least, approaches a constant value in very dilute solution. From these values, Traube has deduced figures which represent the atomic solution volumes and he finds that for a non-electrolyte in aqueous solution the molecular solution volume is equal to the sum of the atomic volumes, *plus* an increment of 12.4 c.c., which is termed the 'molecular co-volume.' He further concludes that the contraction accompanying the dissolution of a gram-molecule of any non-electrolyte in water (a *dilute* solution being formed) is 13.5 c.c. at 15°, and that the contraction for each gram-ion of a binary electrolyte is the same as that for the gram-molecule of a non-electrolyte.

Osmosis and related properties.—If a layer of concentrated sugar solution is put at the bottom of a tall jar and the jar is then carefully filled up with water, diffusion sets in, with the result that the concentration of the sugar ultimately becomes uniform throughout the jar. The existence of the force which thus brings about the intermixture of the sugar and the water could be rendered evident by interposing between solution and solvent some surface which would differentiate between sugar and water, preventing the passage of the former, but freely permeable to the latter. If a membrane with these properties were interposed between the water and the strong sugar solution the system would seek to reach equilibrium in the only way left open to it, viz. by water entering the solution through the membrane; that is, a one-sided diffusion, or 'osmosis,' would occur. The resulting increase in the bulk of the solution would lead

either to the bursting of the membrane or, if the membrane were rigid and strong enough, to the production of a hydrostatic pressure opposing the further passage of water into the solution. The pressure developed in the solution in the latter case might be taken as a measure either of the driving force under the influence of which the sugar molecules diffuse; or, simply, of the attraction between solvent and solution.

These conditions are capable of experimental realisation. Membranes are known which may be described as 'semi-permeable,' since they are freely permeable to water, but practically impermeable to certain dissolved substances. A membrane of copper ferrocyanide, for instance, produced at the common surface of solutions of copper sulphate and potassium ferrocyanide, is permeable to water, but impermeable to dextrose or sucrose, and has been much used in the quantitative study of osmosis. When the copper ferrocyanide is deposited in the walls of a porous porcelain pot, sufficient strength and rigidity are imparted to the membrane to enable it to withstand high pressures. The porous pot, connected with a closed mercury manometer, is filled with a solution of dextrose or sucrose, and is then immersed in pure water. The force with which water seeks to enter the solution is then determined by measuring the pressure developed within the cell—the 'osmotic pressure,' as it is called.

The first direct determinations of this force (Pfeffer, Osmotische Untersuchungen, 1877) showed that the osmotic pressure of sucrose solutions at a constant temperature is approximately proportional to the concentration, and that the osmotic pressure of a given sucrose solution varies nearly as the absolute temperature (*see* van't Hoff, Phil. Mag. 1888, 26, 81; Ladenburg, Ber. 1889, 22, 1225; Adie, Chem. Soc. Trans. 1891, 59, 344; König and Hasenbäumer, Zeitsch. angew. Chem. 1909, 22, 1009, 1070). The validity of these relationships has recently been subjected to a searching investigation by Morse, Frazer and others (Amer. Chem. J. 1905, 34, 1; 1906, 36, 1, 39; 1907, 37, 324, 425, 558; 38, 175; 1908, 39, 667; 40, 1, 194; 1909, 41, 1, 257; 1911, 45, 91, 237, 383, 517, 554; J. Amer. Chem. Soc. 1916, 38, 1907; 1921, 43, 2501). Working with dextrose and sucrose solutions containing from 0.1 to 1.0 gram-molecule per 1000 grms. of water, these investigators find that the osmotic pressure is proportional to the concentration, provided that this latter is referred, not to unit volume of the solution, but to unit volume of the solvent. For the temperature range 0°–25°, they find that the osmotic pressure of a given solution is proportional to the absolute temperature.

Direct determinations of the osmotic pressure of concentrated solutions have been made by Lord Berkeley and co-workers (Phil. Trans. A, 1906, 206, 481; 1909, 209, 177, 319; *see* also Proc. Roy. Soc. A, 1909, 82, 271). They have investigated sucrose solutions containing up to 750 grms. sucrose per litre and measured osmotic pressures up to 133 atmospheres. It is found that the osmotic pressure increases more rapidly than the concentration, even when the latter is referred to unit volume of the solvent. (For reviews and discussions of osmotic pressure, *see* Lowry, Science Progress, 1913, 7, 544; Findlay's

monograph on 'Osmotic Pressure'; Trans. Faraday Soc. 1917, 13, 156-189.)

For the purpose of finding 'isotonic' solutions—that is, solutions of equal osmotic pressure—a study of the water exchange taking place across a semi-permeable membrane of animal or vegetable origin has been found useful (*see*, for instance, Tammann, *Ann. Physik*, 1888, 34, 299; de Vries, *Zeitsch. physikal. Chem.* 1888, 2, 415; Hamburger, *ibid.* 1890, 6, 319; Hedin, *ibid.* 1895, 17, 164). One chief result of these investigations has been to show that, for equal molecular concentrations, the osmotic activity of a binary salt (*e.g.* sodium chloride) is much greater than that of a non-electrolyte such as sucrose, and that ternary salts (*e.g.* calcium chloride) are still more active.

The vapour pressure p' of a solution of a non-volatile solute is lower than the vapour pressure p of the pure solvent at the same temperature, and the relation between these and the concentration is expressed by the formula $\frac{p-p'}{p} = \frac{n}{n+N}$,

where n and N are the numbers of gram-molecules of solute and solvent respectively in the solution (*see* Raoult, *Zeitsch. physikal. Chem.* 1888, 2, 353). There is also a quantitative relationship between the osmotic pressure of a solution and its vapour pressure (van't Hoff, *ibid.* 1887, 1, 481; Gouy and Chaperon, *Ann. Chim. Phys.* 1888, 13, 124; Arrhenius, *Zeitsch. physikal. Chem.* 1889, 3, 115; Berkeley and Hartley, *Proc. Roy. Soc. A*, 1906, 77, 156; Spens, *ibid.* 234; Porter, *ibid.* 1907, 79, 519; 1908, 80, 457). In order to deduce osmotic pressure from vapour pressure by this relationship it is necessary to know only the *ratio* of the vapour pressures of solvent and solution at the same temperature, not their absolute values. The value of the ratio can be found by Ostwald and Walker's method (*Zeitsch. physikal. Chem.* 1888, 2, 602), and Berkeley and Hartley, using a modified form of apparatus, have found that the values of the osmotic pressure deduced from the relative vapour pressures of solvent and solution are in good agreement with the values obtained by direct measurement (*Proc. Roy. Soc. A*, 1906, 77, 156; *Phil. Trans. A*, 1909, 209, 177; 1919, 218, 295). For measurements of the vapour pressure of concentrated aqueous solutions by static methods, *see* Applebey and Hughes, *Chem. Soc. Trans.* 1915, 107, 1798; Wood, *Trans. Faraday Soc.* 1915, 11, 29; Frazer and others, *J. Amer. Chem. Soc.* 1914, 36, 2439; 1916, 38, 515.

The boiling-point of a solution of a non-volatile solute is higher than that of the pure solvent, the extent of the rise being proportional to the molecular concentration of the solute (Raoult, *Compt. rend.* 1878, 87, 167; Beckmann, *Zeitsch. physikal. Chem.* 1889, 4, 532; 1890, 6, 437; 1891, 8, 223; 1894, 15, 656; compare, for other practical methods of finding the rise of boiling-point for a solution: Sakurai, *Chem. Soc. Trans.* 1892, 61, 989; Landsberger, *Ber.* 1898, 31, 458; Walker and Lumsden, *Chem. Soc. Trans.* 1898, 73, 502; Turner, *ibid.* 1910, 97, 1184; Cottrell, *J. Amer. Chem. Soc.* 1919, 41, 721). For each solvent there is a characteristic figure or constant, known as the 'molecular elevation of the boiling-point,' which is defined

as the rise of boiling-point for a solution containing 1 gram-molecule of solute in 100 grms. of solvent. This constant can be evaluated either empirically, from the rise of boiling-point observed with normal solutes of known molecular weight, or from van't Hoff's formula $k=0.02T^2/l$, where T is the boiling-point of the solvent on the absolute scale, and l is its latent heat of vaporisation.

The osmotic pressure P of a moderately dilute solution can be calculated from its boiling-point T by the formula $P = \frac{1000Sl}{24.25} \cdot \frac{T-T_0}{T_0}$ atmospheres, where S is the sp.gr. of the solvent at its boiling-point T_0 , and l is the latent heat of vaporisation for 1 grm. of solvent. For aqueous solutions this formula reduces to $P = 56.8 (T - T_0)$ atmospheres.

The freezing-point of a solution is lower than that of the pure solvent by an extent which is proportional to the molecular concentration of the dissolved substance (for details of this, *see* CRYOSCOPY). The osmotic pressure P of a solution is quantitatively related to its freezing-point

T by the formula $P = \frac{1000Sw}{24.25} \cdot \frac{T_0 - T}{T_0}$ atmospheres, where S is the sp.gr. of the solvent at its freezing-point T_0 , and w is the latent heat of fusion for 1 grm. solvent. For aqueous solutions this formula becomes $P = 12.03 (T_0 - T)$ atmospheres.

The quantitative relationships already referred to between osmotic pressure, lowering of vapour pressure, rise of boiling-point, and depression of freezing-point, on the one hand, and molecular concentration on the other, are, generally speaking, valid only for solutions of non-electrolytes. For electrolytic solutions, notably those of salts in water, the osmotic value, determined directly or indirectly, is abnormally high. The observed depression of freezing-point, for instance, for a dilute solution of sodium chloride in water is nearly twice as great as the depression calculated from the accepted freezing-point constant for water, on the assumption that the molecular condition of the dissolved salt is represented by NaCl. If

$i = \frac{\text{observed depression}}{\text{theoretical depression}}$, it is found that for

dilute solutions of binary salts, such as sodium chloride, the values of i run up to 2, while for dilute solutions of ternary salts, such as calcium chloride, the values run up to 3 (*see* Arrhenius, *Zeitsch. physikal. Chem.* 1887, 1, 635; 1888, 2, 495; Bedford, *Proc. Roy. Soc. A*, 1910, 83, 454; Noyes and Falk, *J. Amer. Chem. Soc.*, 1910, 32, 1011). It is noteworthy that for solutions of sodium mellitate a value of i almost equal to 6 has been recorded (Taylor, *Zeitsch. physikal. Chem.* 1898, 27, 361).

Electrical conductivity.—The significance of this property in relation to the constitution of solutions is generally admitted. The accurate determination of the electrical conductivity of aqueous salt solutions dates from the investigations of Kohlrausch (*Ann. Physik*, 1879, 6, 1, 145; 1885, 26, 161; *see* especially Kohlrausch and Holborn, 'Leitvermögen der Elektrolyte,' 1898, where there is a full list of references to all the fundamental work on the subject; *also* Kraus, 'The Properties of Electrically Conducting Systems,' 1922). These, supported by

the work of later investigators, have shown that whilst for a given salt the conductivity referred to standard dimensions of the conducting column diminishes as the dilution increases, on the other hand the conductivity referred to a fixed quantity of the dissolved salt *increases* with the dilution. The 'specific resistance' of an electrolytic solution is now defined as the resistance in ohms between two opposite faces of a centimetre cube containing the solution. The 'specific conductivity,' represented by the symbol κ , is the reciprocal of the specific resistance, and diminishes as the dilution increases. A measure of the conductivity referred to a fixed quantity of the dissolved electrolyte is given by the product $\kappa \times \phi$, where ϕ is the volume of solution (in cub. cms.) containing 1 gram-equivalent of the solute. The product $\kappa \times \phi$ is represented by the symbol Λ (or λ) and is termed the 'equivalent conductivity.' The equivalent conductivity of a salt (acids and bases included) increases as the concentration diminishes, and approaches a maximum limit at very high dilutions. In many cases at least, an extrapolation may be made and the limiting value Λ_∞ of the equivalent conductivity at infinite dilution thus obtained (see Kohlrausch, *Ann. Physik*, 1885, 26, 161; Bredig, *Zeitsch. physikal. Chem.* 1894, 13, 191). The variation of specific and equivalent conductivity with dilution for non-aqueous solutions appears to be generally of the same character as for aqueous solutions (see Walden, *ibid.* 1906, 54, 133; 1911, 78, 257; Turner, *Amer. Chem. J.* 1908, 40, 571; Philip and Courtman, *Chem. Soc. Trans.* 1910, 97, 1261; Walden, 'Elektrochemie nichtwässriger Lösungen,' 1923).

The values of Λ_∞ for aqueous solutions, more particularly those of binary electrolytes, were shown by Kohlrausch to be additive in character; that is, Λ_∞ may be represented as the sum of two other values, attributable to the positive and negative ions respectively. The equation $\Lambda_\infty = u + v$, where u is the contribution of the cation and v is that of the anion, is the algebraic expression of Kohlrausch's Law of the Independent Migration of the Ions, for it is found that the contribution which any ion makes to the equivalent conductivity at infinite dilution is independent of the other ion with which it is associated (see Kohlrausch, *l.c.*; Loeb and Nernst, *Zeitsch. physikal. Chem.* 1888, 2, 948). The actual values of u and v are obtained by a combination of the figures for Λ_∞ with Hittorf's transport numbers (Pogg. *Ann.* 1853, 89, 177; 1856, 98, 1; 1858, 103, 1; 1859, 106, 338, 513; reprinted in Ostwald's *Klassiker der Exakten Wissenschaften*: see also Loeb and Nernst, *l.c.*; Drucker, *Zeitsch. Elektrochem.* 1907, 13, 81; Kohlrausch, *ibid.* 333; McBain, *Proc. Wash. Acad. Sci.* 1907, 9, 1; Washburn, *Technology Quart.* 1908, 21, 164; Denison, *Trans. Faraday Soc.* 1909, 5, 165). The relation between the conductivity and the viscosity of salt solutions also has an important bearing on their constitution (see Kohlrausch, *Sitzungsber. K. Akad. Berlin*, 1902, 572; Bousfield and Lowry, *Proc. Roy. Soc.* 1902, 71, 42; Walden, *Zeitsch. physikal. Chem.* 1906, 55, 207; 1911, 78, 257).

Theories of solution.—The remarkable way

in which physical and chemical conceptions of the relation between solute and solvent have long struggled for pre-eminence has been sketched in detail by Walden (Ahrens' *Sammlung*, vol. 15: 'Die Lösungstheorien in ihrer geschichtlichen Aufeinanderfolge'). The last three decades have witnessed a renewed activity in the investigation of solutions, resulting in the accumulation of a vast amount of material, some part of which has been indicated in the preceding paragraphs. Some scientists have interpreted these facts in terms of a chemical interaction of solute and solvent: by others, physical considerations have been put in the foreground, to the exclusion of any chemical factor.

The 'hydrate' theory is based on the view that the formation of an aqueous solution is essentially a process of association, and that the solution contains compounds of solute and solvent, the complexity of which increases with dilution. The supporters of this theory originally found evidence for their views in the character of the density-concentration curves (see Mendeléeff, *Zeitsch. physikal. Chem.* 1887, 1, 273; *Chem. Soc. Trans.* 1887, 51, 778; Pickering, *ibid.* 1890, 57, 64; Watts' *Dictionary*, 1894, 'Solution,' second article). The method, however, adopted for deducing the composition of the definite hydrates supposed to be present in the solutions has been subjected to serious criticism, and in its original form the theory is hardly tenable. If modified in harmony with the conceptions of reversibility and mass action a hydrate theory of solution has many facts in its favour (see Lowry, *Science Progress*, 1908, 3, 124). The case in support of the view which regards the solvent as exercising an associative function has been stated also by Armstrong (*Proc. Roy. Soc. A*, 1906, 78, 264; *ibid.* 1908, 81, 80; *Chem. News*, 1911, 103, 97).

More generally accepted at the present time and more commonly employed as a working hypothesis in the investigation of solutions are the theories associated with the names of van't Hoff and Arrhenius. By a thermodynamical argument, based on the validity of Henry's Law, van't Hoff reached the conclusion that the osmotic pressure of a dilute solution must be proportional (1) to the concentration of the solute, and (2) to the absolute temperature (*Zeitsch. physikal. Chem.* 1887, 1, 481; *Phil. Mag.* 1888, 26, 81; compare Rayleigh, *Nature*, 1897, 55, 253; Kelvin, *ibid.* 272; Larmor, *ibid.* 545). He pointed to Pfeffer's measurements (see above) as an experimental verification of these conclusions, and therefore felt justified in extending Boyle's Law and Gay-Lussac's Law to dilute solutions. Further, van't Hoff extended Avogadro's hypothesis to solutions and assumed that at a given temperature equal volumes of two dilute solutions which have equal osmotic pressures contain the same number of dissolved molecules. Evidence in favour of this extension of Avogadro's hypothesis was found in the known influence of different substances on the vapour pressure and freezing-point of a solvent. In analogy then with the gas equation $pv = RT$, the behaviour of substances in dilute solution may be represented by an equation $PV = R'T$, where P is the osmotic pressure and V is the volume of solution

containing 1 gram-molecule of solute. The known values of P , V , and T , for dilute sucrose solutions showed that $R'=R$, and hence van't Hoff concluded that the osmotic pressure of a dilute sugar solution is equal to the pressure which the sugar would exert if it were in the gaseous state at the same temperature and occupied the same volume as the solution. While this statement is valid for dilute solutions it is not strictly accurate for higher concentrations. Under these conditions the observed osmotic pressure for sucrose solutions is greater than the corresponding gas pressure, even when the concentration is referred to unit volume of solvent instead of unit volume of solution (see Morse and others, *Amer. Chem. J.* 1911, 45, 554; Berkeley and Hartley, *Phil. Trans. A*, 1906, 206, 481; Berkeley, *Proc. Roy. Soc. A*, 1907, 79, 125; Callendar, *ibid.* 1908, 80, 466).

It should be noted that the quantitative relationships involved in van't Hoff's theory are independent of the exact way in which the osmotic pressure originates. Indeed, diverse views are held as to the origin and mechanism of osmotic pressure (see, for instance, Bredig, *Zeitsch. physikal. Chem.* 1889, 4, 444; L. Meyer, *ibid.* 1890, 5, 23; van't Hoff, *ibid.* 1890, 5, 174; Ber. 1894, 27, 6; Whetham, *Nature*, 1896, 54, 571; Poynting, *ibid.* 55, 33; Armstrong, *ibid.* 55, 78; Barmwater, *Zeitsch. physikal. Chem.* 1899, 28, 115; Lowry, Kahlenberg and others, *Trans. Faraday Soc.* 1907, 3, 14; Traube, *Ber.* 1909, 42, 86).

In his original paper, van't Hoff drew attention to the fact (see above) that there are certain substances which in aqueous solution give abnormally high osmotic pressures and the behaviour of which cannot be represented by the formula $PV=RT$. These exceptional cases are very numerous, but can be brought into line with normal substances by assuming that the abnormal substances are dissociated. Arrhenius had pointed out that it is precisely those substances (viz. salts, acids and bases) which give abnormally high osmotic values in aqueous solution that make water a conductor of the electric current, and he proposed a common explanation for the two phenomena by suggesting that when a salt is dissolved in water it dissociates to a greater or less extent into positively and negatively charged particles or ions. Such a dissociation would mean an increased number of units in solution and so would account for the abnormally high osmotic values observed with salt solutions. The presence of the ions would confer on the water the power of conducting the electric current, the passage of the current through a conductor of this kind being supposed to consist in the streaming of positive ions in the one direction and of negative ions in the other, under the influence of the applied E.M.F.

In relation to conduction, Arrhenius classified the molecules in a salt solution as active or inactive, according as their ions were independent in their movements or were closely linked together. Only the active molecules were able to take part in the conduction of the current, but it was supposed, in view of the variation of equivalent conductivity with concentration, that at extreme (infinite) dilution all the mole-

cules of the dissolved salt became active. On this basis, a measure of the extent of dissociation in any salt solution is obtained by comparing the value Λ of the equivalent conductivity for that solution with the value Λ_∞ of the equivalent conductivity at infinite dilution. If α is the 'degree of dissociation' (or 'coefficient of ionisation') then $\alpha = \frac{\Lambda}{\Lambda_\infty}$. On the other hand,

if i is a measure of the osmotic abnormality (see above), it follows that $\alpha = \frac{i-1}{n-1}$, where n is the

number of ions into which a molecule of solute dissociates. Arrhenius showed that the values of α deduced for a given salt by the two methods were in fair agreement (Arrhenius, *Zeitsch. physikal. Chem.* 1887, 1, 631; 1888, 2, 495; Watts' Dictionary, 1894, 'Solution,' first article; Whetham, *Proc. Roy. Soc.* 1900, 66, 192; Noyes, *Technology Quart.* 1904, 17, 293; Drucker, 'Die Anomalie der starken Electrolyte,' *Ahrens' Sammlung*, 1905; Bedford, *Proc. Roy. Soc. A*, 1910, 83, 454; Noyes and Falk, *J. Amer. Chem. Soc.*, 1912, 34, 485).

It should be noted, in passing, that several investigators, in interpreting the behaviour of solutions, more especially of the so-called strong electrolytes, start with the assumption of complete, instead of partial, dissociation (Milner, *Phil. Mag.* 1912, 23, 553; 1913, 25, 742; Bjerrum, *Zeitsch. Elektrochem.* 1918, 24, 321; Ghosh, *Chem. Soc. Trans.* 1918, 449, 627, 707; Brönsted, *J. Amer. Chem. Soc.* 1920, 42, 761; *Chem. Soc. Trans.* 1921, 119, 574).

The electrolytic dissociation theory of Arrhenius has proved very serviceable in the quantitative study of numerous phenomena exhibited by aqueous solutions of acids, bases and salts; as, for instance, in the interpretation of diffusion (Nernst, *Zeitsch. physikal. Chem.* 1888, 2, 613; 1889, 4, 129; Arrhenius, *ibid.* 1892, 10, 51), of the relative strength of acids and bases (Ostwald, *ibid.* 1888, 2, 36, 270; van't Hoff and Reicher, *ibid.* 779; Arrhenius, *ibid.* 1889, 4, 226; Walker, *ibid.* 319; Shields, *Phil. Mag.* 1893, 35, 365), of the influence of salts on the activity of the corresponding acids (Arrhenius, *Zeitsch. physikal. Chem.* 1888, 2, 284; 1890, 5, 1), of reciprocal solubility influences (Nernst, *ibid.* 1889, 4, 372; Noyes and others, *ibid.* 1890, 6, 241; 1892, 9, 603; 1898, 27, 267, 442), of the distribution of an electrolyte between two immiscible solvents (Nernst, *Zeitsch. physikal. Chem.* 1891, 8, 110), and of the thermo-chemistry of salt solutions (Arrhenius, *Zeitsch. physikal. Chem.* 1889, 4, 96; 'Theories of Chemistry,' 1907, chap. xiii.).

The fact that water is such a good dissociating or ionising solvent is probably connected with its high dielectric constant (Thomson, *Phil. Mag.* 1893, 36, 320; Nernst, *Zeitsch. physikal. Chem.* 1894, 13, 531; Walden, *ibid.* 1906, 54, 129; compare Crompton, *Chem. Soc. Trans.* 1897, 71, 925; Dutoit and Friderich, *Bull. Soc. chim.* 1898, 19, 321; Dutoit and Aston, *Compt. rend.* 1898, 125, 240; Brühl, *Zeitsch. physikal. Chem.* 1898, 27, 319). This, however, does not adequately explain the cause of ionisation, or indicate the source whence the energy necessary for ionisation is derived. It has been growingly felt that in the earlier presentation and applications of the theory of electrolytic dissociation

the part played by the solvent was too much neglected, and at the present time the view is commonly held that, in many cases at least, the ions of a salt solution are hydrated. Not only so; it is urged by some that it is the hydration of the ions which is the source of energy in ionisation (*see* Lowry, *Science Progress*, 1908, 3, 202; Kendall and Booge, *J. Amer. Chem. Soc.* 1917, 39, 2323; Kendall, *Proc. Nat. Acad. Sci.* 1921, 7, 56). The evidence bearing on the existence of hydrated ions and the methods available for determining the extent of hydration have been summarised by Washburn (*Technology Quart.* 1908, 21, 360).

J. C. P.

SOLVEOL. A solution of cresol in sodium cresotinate. Used as an antiseptic.

SOMATOSE. An albumose preparation from meat.

SOMBRERITE. A mixed calcium and aluminium phosphate occurring on Sombrero and other islands of the Antilles (*v.* FERTILISERS; also PHOSPHORUS).

SOMNAL. An ethylated derivative of chloral urethane. Used as a hypnotic.

SOMNIFENE. Diethylamine diethyl-dipropenyl barbiturate. Used as a hypnotic.

SOMNOFORM. A mixture of ethyl chloride or bromide with chloroform. Used as an anæsthetic.

SOPHOL. Syn. for silver formonucleinate.

SOPHORA JAPONICA (Linn.). A large and beautiful tree, not unlike an acacia, belonging to the *Leguminosæ*, which grows abundantly throughout China.

The undeveloped flower buds furnish yellow dyestuff at one time largely employed by the Chinese for colouring the silken vestments of the mandarins. For this purpose the buds were collected and dried rapidly, either in the sun or by artificial means, usually with the addition of a little chalk. The method of dyeing consists in simply boiling for 1–1½ hours in a decoction of the flower buds, silk which has been previously mordanted by steeping overnight in a decoction of alum. Less frequently it is employed in the dyeing of cotton and wool. Its price appears to be about 30s. a cwt.

This dyestuff has been studied by many chemists, especially by Schunck (*Chem. Soc. Trans.* 1888, 53, 262; 1895, 67, 30), who has proved that the glucoside which it contains formerly called sophorin (Förster, *Ber.* 1882, 15, 214) is in reality identical with rutin, the quercetin glucoside first isolated from rue (*Ruta graveolens* [Linn.]) by Weiss (*Chem. Zentr.* 1842, 903). (Compare also Stein, *J. pr. Chem.* [i.] 58, 399; 85, 351; 88, 280; Schunck, *Manchester Memoirs*, 1858, 2 ser. 15, 122.)

The glucoside is readily isolated by extracting the flower buds with boiling water. The liquid on cooling deposits crystals of rutin which can be purified by recrystallisation from water or dilute alcohol.

When applied to wool the *Sophora Japonica* buds give colours somewhat like those obtained with quercitron bark, viz. a dull orange with chromium, a yellow of moderate brilliancy with aluminium, a bright yellow with tin, and a dark olive with iron. In dyeing power it seems to be equal if not slightly superior to quercitron bark,

and is to be regarded as an excellent natural dyestuff, quite equal to those of similar character in general use (Hummel and Perkin, *J. Soc. Chem. Ind.* 1895, 458).

A. G. P.

SOPHORINE *v.* CYTISINE and RUTIN.

SORANJES, or **SURANJI**, *v.* AAL.

SORBITE. One of the constituents of steel. It is intermediate in properties between cementite and pearlite (*q.v.*), and may be regarded as pearlite in which the lamellæ or granules are so fine that no microscope can resolve them (Osmond, *Revue de Métallurgie*, 1904).

It is an important constituent of structural steels, *v.* METALLOGRAPHY.

SORBITOL *v.* CARBOHYDRATES.

SORBOSE *v.* CARBOHYDRATES.

SORGHUM BEER. A variety of beer manufactured in Matabele from Sorghum or Kaffir corn (*Andropogon sorghum*). A mixture of water and flour, prepared from the unmalted cereal, is boiled in earthen vessels and exposed to the air for 24 hours, after which malted sorghum flour is added in the proportion of 1 part to 3 parts of the unmalted flour. The starch present is partially transformed into dextrose, and this sugar is rapidly fermented by yeasts derived from the air. Fermentation is at a maximum in about 16 hours, when a thick yellow scum rises to the surface, and after two days the liquid is filtered through bags of plaited rush and is consumed on the day following. Analysis of the product yielded the following results: Apparent gravity, 1011; alcohol, 2.91; extractives, 4.2; maltose, 0.26; acidity, 0.35 p.c., together with a large proportion of unconverted starch. The beverage is of an agreeable flavour but deteriorates rapidly, and cannot be kept (*Journal of the Institute of Brewing*, June, 1923, Abstracts, p. 479, from *Bulletin Assoc. Chim. de Sucrerie*, 1922, 40, 163).

Starch is largely responsible for the jellying of sorghum syrup and for the extreme difficulty in filtering sorghum juice, especially after it has been heated. Preliminary treatment of the juice with malt diastase greatly increases the rate of filtration and prevents the jellying of the finished syrup. By boiling and filtering the syrup the formation of scums during subsequent concentration is almost entirely prevented. There was no appreciable difference in flavour, appearance, or sugar content in the syrup from the treated and untreated juice (*S. F. Sherwood, J. Ind. Eng. Chem.* 1923, 15, 780–782; *J. Soc. Chem. Ind.* 1923, 42, 941 A.).

SUDAN BROWN *v.* AZO-COLOURING MATTERS.

SOUTH AFRICAN BUSH TEA. The dried leaves and tops of several species of *Cyclopia*; *C. subternata*, Vog.; *C. latifolia*, D.C.; *C. genistoides*, Vent.; and *C. sessiliflora*, Eckl. and Zeyh. Used at Cape Colony as a substitute for tea. Contains no theine. (*Cf.* Greenish, *Pharm. J.* 1881.)

SOY. A well-known sauce made from soy beans (*Soja hispida* (Moench.); nat. ord. *Leguminosæ*), chiefly in Japan, and to a less extent in China, India, and the Moluccas. It is known to the Japanese as 'Sho-ju,' and to the Dutch, by whom it appears to have been introduced into Europe, as 'shoya.'

To prepare the sauce, the beans are ground

up with an equal quantity of wheat or barley, and boiled with water until soft, when the mixture is left in a warm place for about 24 hours to ferment. It is then covered with a thick layer of salt, water poured over it, and the mass stirred daily for about a couple of months. The liquor is then poured off, squeezed out of the sediment and stored in wooden vessels, in which it clears on standing.

A Chinese sauce, known as 'kit-jap' (hence 'ketchup'), is sometimes sold as 'soy,' and often the article described under this name is nothing more than diluted molasses flavoured to imitate soy. For an account of the Japanese Soy industry, see Kita, J. Soc. Chem. Ind. 1913, 32, 1081. J. C.

SOYA (Soja) BEAN OIL (*Soy-Bean oil, Bean oil, Chinese Bean oil*). This oil is obtained from the seeds of *Glycine soja*, Sieb. et Zucc., *Dolichos soja*, Linn., *Soja hispida*, Moench, *Soja japonica* Savi, *Glycine hispida*, Maxim ('Sachuca bean'), a plant indigenous to China, Manchuria, Korea, Japan, Formosa, Java, and Indo-China, where the oil and the expressed cake have been largely used as foodstuffs for upwards of two thousand years. The name is derived from the Japanese word 'Sho-ju,' a kind of sauce made from the bean. The seeds contain 18 p.c. of oil and about 30-40 p.c. of proteins.

The cultivation of the soya bean has been for centuries the main agricultural industry of Manchuria, and the industries based on the production of soya bean oil and soya bean cake have formed the most important manufacture of Manchuria, and to a large extent of Japan. The annual production in Manchuria is stated to be about 1,850,000 metric tons, of which 75 p.c. is exported. Up to the Russian-Japanese war, the soya bean and soya bean oil were practically unknown in Europe. Since then, however, enormous quantities have been imported into Europe and the oil has in an extremely short time acquired the position of one of the foremost oleaginous seeds, the industry rivalling in extent and importance the cotton-seed oil industry of Europe. Owing to their high proportion of proteins, the seeds have rapidly acquired great commercial importance; especially so as it is stated that the soya cake is instrumental in producing cow-milk richer in butter fat than is obtained when feeding with linseed and cotton-seed cake. In this country, however, the cake has not yet been employed for feeding milk cows to the same extent that it has on the Continent (Denmark, Holland).

In this connection it may be mentioned that an artificial milk prepared from soya beans is now a regular article of commerce. It is yellowish white in colour, and has a sickly sweet taste and a faintly acid reaction. A sample consisted of water 88.93 p.c., dry matter 11.07, fat 3.06, non-fatty solids 8.01, proteins 2.96, starch 0.57, glucose 2.48, mineral matter 0.63, alkalinity of ash 6.44 c.c. of N/1 acid. The gross energy content was 54 cal. (cow's milk 70 cal.). Content of food units 27 (cow's milk 34). Hence it is not an economical substitute for cow's milk, unless the price of the soya bean milk is considerably less than that of cow's milk (Remy, Zeitsch. Nahr. Genussm. 1922, 43, 380). Soya bean milk is sometimes added to cow's milk in countries, as in Japan,

where the bean milk is a common article of commerce. It may be detected by adding 4 or 5 drops of a 28 p.c. solution of potassium hydroxide to 10 c.c. of the milk when a yellow colour is produced, due to the action of the potassium hydroxide upon glycinine, the main constituent of soya bean protein (Nakayasu, J. Pharm. Soc. Japan, 1921, 476, 880).

The mean analysis of nine samples of black and yellow soya beans from different parts of Bulgaria was: water 10.91 p.c., protein 36.76, fat 18.57, nitrogen-free extract 25.27, crude fibre 3.94, ash 4.75. Samples of artificial milk prepared from Bulgarian soya beans gave: water 90.53-88.19 p.c., protein 5.3-6.04, fat 2.21-2.94, carbohydrates 1.18-1.90, ash 0.78-0.93 (Zlataroff and Trifonow, Zeitsch. Nahr. Genussm. 1922, 44, 216; J. Soc. Chem. Ind. 1923, 67 A.).

Baughman and Jamieson (J. Amer. Chem. Soc. 1922, 44, 2947) state the chemical composition of soya bean oil as follows: d_{25}^{25} 0.9203, n_D^{20} 1.4736, iodine value (Hanus) 128.0, saponif. number 189.5, acid number 0.5, acetyl value 17.0, Reichert-Meissl value 0.16, Polenske value 0.26, unsapon. matter 0.6 p.c., saturated acids 11.5, unsat. acids 83.5. Detailed analysis showed its composition to be: glycerides of linolenic acid 2.3 p.c., of linolic acid 51.5, of oleic acid 33.4, of palmitic acid 6.8, of stearic acid 4.4, of arachidic acid 0.7, of lignoceric acid 0.1, and 0.6 unsapon. matter. Total 99.8 p.c.

In Manchuria, four varieties of Soja are known commercially, namely, yellow, green, blue, and black, but the commercial seeds represent very many varieties, at least thirty in number. The almost phenomenal importance which the soya bean industry acquired in the course of two years has led to the attempt to cultivate the soya bean for commercial purposes in other countries, and at present experiments are being made to produce soya beans in Australia, South Africa, United States of America, Italy, Spain, South America, and even in this country.

In Manchuria, the beans are soaked in water over night, then crushed and boiled with a little water so as to burst the oil cells. The oil, which exists to the amount of 18 to 21 p.c., is then expressed in the most primitive fashion; but owing to the long time the cakes are allowed to remain in the press the yield of oil amounts to 13 p.c., whereas experiments made with modern machinery are stated to have yielded no more than 10 p.c. The expressed meal is made into bean-cakes which constitute one of the staple foods of the country, and form the most important article of export. Before the Russian-Japanese war, the chief export of beans from Manchuria was to Japan, where the bean is used on the most extensive scale for the preparation of the condiment 'Shoyu' and 'Miso' (Soja sauce). In both these forms the bean, together with other cereals, is subjected to fermentation with yeast (kôji). Other preparations are tôfu, coagulated soya protein pressed into a moist cake, and 'Natto,' the fermented bean used as a substitute for cheese, and as an ingredient in the manufacture of chocolate, biscuits and bread, and as a food for diabetics. The waste from the pressed beans is largely used as cattle food and as manure for

the rice-fields. For the manufacture of the plastic products from the protein of soya beans, see S. Satow (Tech. Rep. of the Tohoku Imperial University, 1923, 3, No. 4, 69 pp.).

For the characteristics of soya bean oil, see OILS, FIXED, AND FATS.

The oil must be classed with the drying oils, inasmuch as it (or at least some varieties of the soya bean oil) yields up to 5 p.c. of insoluble bromide in the bromide test. The drying powers are, however, not so pronounced as those of linseed oil, although the oil from certain varieties of beans can be used as a substitute for linseed oil. When blown with dry air soya bean oil thickens and attains a sp.gr. exceeding 0.960. Blown soya bean oil is used in the manufacture of linoleum. It is also employed in an increasing amount in the manufacture of soap, paints, varnishes, and as a rubber substitute, and to some extent as an hydrogenated oil. The mixed fatty acids obtained from soya bean oil with an iodine value of 134 were found to be as follows: linolenic acid 2-3 p.c., linolic acid 55-57, oleic acid 26-27, saturated fatty acids 9-10 (Smith, J. Ind. Eng. Chem. 1922, 14, 530). See Researches on Oil and Proteids extraction from Soy Bean, by Sadakichi Satow, Technology Reports of the Tohoku Imperial University, Sendai, Japan, 1921. For the Manufacture of Plastic Products from Proteid of Soy Bean, by Sadakichi Satow, see The Technology Reports of the Tohoku Imperial University, Sendai, Japan, vol. iii. No. 4, 1923. See also Soybean, Piper and Morse, McGraw-Hill, Publishing Co., Ltd.

The hydrogenation of soya bean oil is carried out using catalysts obtained by the reduction of nickel silicate, borate, molybdate, tungstate, chromate, and manganate. Olive oil, corn (maize) oil, neat's foot oil, and a fish oil, and oleic acid and the free fatty acids from cotton-seed, soya bean, fish, and neat's foot oils are also hydrogenated with the nickel silicate catalyst. Nickel silicate proved to be the most active catalyst among those tested in the hydrogenation of cotton-seed oil. The best temperature for the reduction of this catalyst is 290°-300°, and for hydrogenation of the oils 180°-200°. Nickel tungstate is found to be efficient in the hydrogenation of cotton-seed oil, but it requires rather a high temperature for its reduction. Iron retards the catalytic activity of nickel when both these metals are present in the catalyst. Hydrogenation of soya bean oil is very difficult, but may be accomplished by means of nickel chromate or manganate, the iodine value of the oil being reduced to about half its original value. The hydrogenation of free fatty acids is more readily accomplished than that of the corresponding glycerides. The case of neat's foot oil is an especially striking example of this fact (L. Kahlenberg and T. P. Pi, J. Phys. Chem. 1923, 28, 59; J. Soc. Chem. Ind. 1924, 43, B. 184).

Soya bean miso.—Miso is a staple Japanese food made from polished rice fermented with *Aspergillus oryzae*, mixed with steamed soya beans, salt, and water. The oil has the same odour and taste as soya bean oil and the following characters: *d* 0.9466-0.9471, acid value 22.5-77.7, saponif. value 211-235, iodine value 117-132, Hehner value 93.5-98.0, Reichert-Meissl

value 3.56-7.46. The decolorisation of the oil with animal charcoal materially alters the above characters; the iodine value is greatly decreased, and the saponif. and Hehner values are increased, the oil becoming nearly solid. The oil shows a greater Reichert-Meissl value and a smaller iodine value than soya bean oil (R. Kodama, J. Ind. Eng. Chem. 1924, 16, 523; J. Soc. Chem. Ind. 1924, 43, B. 564).

SOZAL *v.* SYNTHETIC DRUGS.

SOZOIODOL. Sozoiodol is the generic name adopted for salts of diiodo-para-phenol-sulphonic acid, $C_6H_2I_2OHSO_3H$; it occurs as a white, glistening, crystalline powder, odourless, of slightly acid taste; slightly soluble in cold water, more easily in hot water; readily soluble in glycerin and in alcohol, and employed in 2 to 3 p.c. solution on wounds. It is decomposed on heating to 200° giving off violet vapours. *Sodium sozoiodol* forms colourless, inodorous, crystalline needles, soluble in about 15 parts of water, also soluble in alcohol and in 20 parts of glycerin. It is used internally as an antiseptic and antidiabetic, and externally in syphilitic lesions, gonorrhœa, rhinitis, whooping cough, &c. Externally, in 2 to 8 p.c. solutions, 10 to 25 p.c. powder or ointment, &c. The finely-powdered substance mixed with equal parts of sulphur is employed by insufflation in treating diphtheria, laryngitis, nasal tuberculosis, &c. It is a powerful germicide (Pharm. J. 1921, 346), *v.* SYNTHETIC DRUGS.

SPANISH GRASS *v.* ESPARTO and PAPER.

SPANISH OCHRE. *Burnt Roman Ochre v.* PIGMENTS.

SPAR (Ger. *Spath*, *Spat*). A general term applied to a variety of minerals without metallic lustre which occur as crystals or which cleave into fragments with bright surfaces. Such sparry minerals are well known to miners as the gangue of metallic ores. Several kinds of spar are distinguished by popular names, and the term also enters into certain mineralogical names. For example: Derbyshire-spar (fluor-spar); calc-spar, Iceland-spar, doubly-refracting spar, dog-tooth-spar, and nail-head-spar (calcite); heavy spar (barytes); satin-spar (gypsum and calcite); tabular spar (wollastonite); adamantine spar (corundum); felspar, feldspar; &c. In special trades, however, the term 'spar' is often used for one particular kind of spar.

L. J. S.

SPARASSOL. M.p. 67°-68°, obtained by Wedekind and Fleischer (Ber. 1924, 151) from the fungus *Sparasses ramosa*, is shown to be identical with the methyl ester of everninic acid (2-methyl-4-methoxy-6-hydroxybenzoic acid) isolated by A. S. Pfau (Ber. 1924, 57, 468) from the fungus *Evernia prunastri*. The formula suggested by Wedekind and Fleischer is therefore incorrect. Sparassol does not exist as such in the fungus, but is formed by alcoholysis of the everninic acid present (J. Soc. Chem. Ind. 1924, 43, B. 399).

According to E. Späth and K. Jeschki (Ber. 1924, 57, 471) the constitution of sparassol (*cf. supra*) was proved thus: orcinol was converted into orcylaldehyde by the method of Gattermann and Köbner (Ber. 1899, 32, 278), the aldehyde was then converted into orsellinic acid, and the latter methylated by means of diazomethane to the 4-methyl ether of methyl

orsellinate (methyl 2-methyl-4-methoxy-6-hydroxybenzoate), which melted at 67°–68° and appeared to be identical with Wedekind and Fleischer's 'sparassol'; this was confirmed by the identity of melting-points of the corresponding methyl ethers, nitro-compounds, acetyl derivatives, and the free everninic acids (J. Soc. Chem. Ind. 1924, 43, B. 399).

SPARTEILENE $C_{15}H_{20}$. A colourless, odourless, optically inactive liquid, b.p. 157°–159°, showing a molecular refraction corresponding with the existence of six ethylenic linkings, derived from dimethyl hemisparteilene, $C_{15}H_{21}NMe_2$; oxidised by means of potassium permanganate sparteilene forms an acid $C_{10}H_{10}O_5$, m.p. 300°–305°.

SPARTEINE $C_{15}H_{26}N_2$ (Mills, Chem. Soc. Trans. 15, 1) is the alkaloid of the common broom, *Cytisus Scoparius* (Link), in which it was discovered by Stenhouse (Chem. Soc. Trans. 4, 218). It is produced in greatest quantity during the early part of the life of the plant (Chevalier, Compt. rend. 1910, 150, 1068), and is prepared from broom-tops by adding caustic soda to the aqueous extract and then distilling with steam, or by evaporating the extract to dryness and dissolving out the alkaloid with dilute hydrochloric acid (Stenhouse). 1000 grms. of the plant yield 3 grms. pure product (Houdé, J. Pharm. Chim. [v.] 13, 39). For other methods of extraction, see Houdé, *l.c.*; Kerchmann, Arch. Pharm. [iii.] 9, 209.

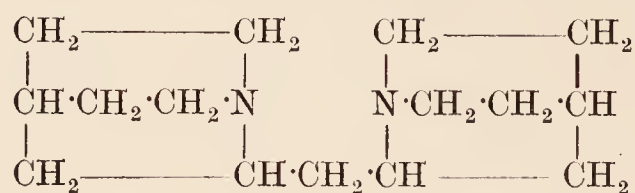
Sparteine is a thick, heavy liquid, colourless when freshly prepared, becoming brown on exposure to light and air. It boils at 180°–181° at 20 mm. (Bernheimer, Gazz. chim. ital. 13, 451); 287° (Houdé); 311°–311.5° at 723 mm. (Bamberger, Annalen, 235, 368); 326° (Wackernagel and Wolfenstein, Ber. 1904, 37, 3238); 188° (corr.) at 18.5 mm. and 235° (corr.) in a current of dry hydrogen at 754 mm. (Moureu and Valeur, Compt. rend. 1903, 137, 194). It has sp.gr. 1.034 at 0°, 1.0196 at 20° (Moureu and Valeur, *l.c.*), 1.0199 at 20° (Semmler, Ber. 1904, 37, 2428); the specific rotation $[\alpha]_D$ is -16.42° (M. and V.), -14.6° at 26° (Bernheimer, *l.c.*); and the refractive index n_D is 1.5293 at 19° (M. & V.), 1.5291 at 20° (Semmler).

It is soluble in water to the extent of 0.304 parts in 100 (Moureu and Valeur, *l.c.*; see also Valeur, Bull. Sci. pharmacol. 1919, 26, 145; Chem. Soc. Abst. 1919, [i.] 454), and is readily soluble in alcohol, ether, and chloroform; insoluble in benzene and petroleum (Houdé, *l.c.*).

Sparteine has a strong alkaline reaction and behaves as a diacid base towards phenol-phthalein, &c., but as a monacid base to litmus. It has a very bitter taste and is a powerful narcotic poison. Administered in small doses (as the sulphate in aqueous solution) it strengthens the action of the heart and immediately regulates any disorder of the cardiac rhythm (Sée, Compt. rend. 101, 1046; see also Maurel, Compt. rend. Soc. Biol. 1903, 55, 1427, and Arch. Experim. Pathol. Pharm. 1892, 141).

Sparteine is a ditertiary base and is completely saturated; it does not contain methyl groups attached to nitrogen (Herzig and Meyer, Monatsh. 1895, 16, 599). On these and other

grounds, the following formula has been proposed by Moureu and Valeur (Compt. rend. 1905, 141, 261, 328; *ibid.* 1912, 154, 309; *ibid.* 1913, 156, 108; Ann. Chim. 1912, [viii.] 245; cf. Germain, Gazz. chim. ital. 1912, 42, [i.] 447):



When oxidised with a strong solution of potassium permanganate or with silver oxide and water in sealed tubes it undergoes profound decomposition, among the products being pyridine, α -picoline and allied compounds (Peratoner, Gazz. chim. ital. 22, 566; Bernheimer, *ibid.* 13, 451; cp. Bamberger, Annalen, 235, 368). Hydrogen peroxide, however, converts it into *oxy*- and *dioxy*-sparteine (Ahrens, Ber. 24, 1095; 25, 3607; 26, 3035; 30, 195; cf. Germain, *l.c.*; Valeur and Luce, Compt. rend. 1919, 168, 1276). The alkaloid *retamine*, obtained from the shoots and bark of *Genista* [*Retama*] *sphaerocarpa* (Lam.), is a hydroxy-sparteine, $C_{15}H_{26}N_2O$, crystallising in long needles, m.p. 162° with decomposition (Battandier and Malosse, Compt. rend. 1897, 125, 360, 450; see also Willstätter and Marx, Ber. 1904, 37, 2351).

Tests for sparteine.—Sodium picrate gives a yellow colour which on addition of sulphuric acid, ammonium persulphate and potassium thiocyanate turns orange-red. If the dry residue obtained by evaporating solutions of ferric chloride and potassium thiocyanate together be touched with a solution containing sparteine an intense bluish-violet coloration is obtained (Reichard, Pharm. Zeit. 48, 385). A solution of bromine in fuming hydrobromic acid forms yellow crystals of *sparteine perbromide*, $C_{15}H_{26}N_2 \cdot 2HBr \cdot Br_2$, m.p. 193°. This reaction will show the presence of sparteine in a dilution of 1 : 10,000 (Corriez).

An aqueous solution of the alkaloid is rendered ammonical and extracted with chloroform; the chloroform solution is shaken with dilute sulphuric acid, the alkaloid again extracted with chloroform after the acid solution has been rendered ammoniacal and the chloroform solution is evaporated. The residue is treated with bromine solution, evaporated to dryness and the residue brought into contact with ammonia gas; a bright red coloration is obtained with as little as 0.0005 gram. of sparteine (Grant, J. Amer. Pharm. Assoc. 1920, 9, 704).

Sparteine sulphate $C_{15}H_{26}N_2 \cdot H_2SO_4 \cdot 5H_2O$, prepared by dissolving the alkaloid in 10 p.c. sulphuric acid and allowing the solution to crystallise in a warm place, forms colourless rhombohedral crystals, soluble in 1.1 parts of water and in 2.4 parts of alcohol at 25°, insoluble in ether and chloroform. In aqueous solution at 15°–20° it has $[\alpha]_D -22.12^\circ$ (Moureu and Valeur, J. Pharm. Chim. 1903, [vi.] 18, 545).

Sparteine hydrochloride and **hydriodide** are white crystalline solids, soluble in water; the latter has m.p. 226°–228°. The *iodobromide* $C_{15}H_{26}N_2 \cdot HI, HBr, H_2O$, faintly-yellow cubical crystals, $[\alpha]_D -16.21'$; *basic hydrobromide* B, HBr [$B = C_{15}H_{26}N_2$], prismatic crystals, m.p.

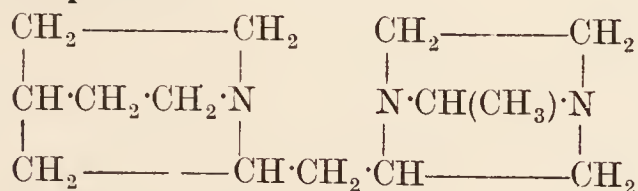
236°, $[\alpha]_D -16^\circ 6'$; *diiodide* $B, 2HI, H_2O$, m.p. (anhydrous) 225°, $[\alpha]_D -16^\circ 2'$; *normal chlorate* $B, 2HClO_3$, colourless cubes, explodes at 147°, $[\alpha]_D -23^\circ 12'$; *basic chlorate* $B, HClO_3$, colourless prisms, explodes at 200°–205°, $[\alpha]_D -16^\circ 3'$; *normal perchlorate* $B, 2HClO_4, 2H_2O$, prisms, m.p. (anhydrous) 265°, explodes over 300°, $[\alpha]_D -17^\circ 30'$; *basic perchlorate* $B, HClO_4$, m.p. 171°, $[\alpha]_D$ in methyl alcohol $-17^\circ 6'$, in acetone $-16^\circ 3'$; *dichromate* $B, H_2C_2O_7$, orange-yellow prisms, decomposes at 128°–129°; *normal salicylate* $B, 2C_7H_6O_3, H_2O$, pale pink prisms, m.p. 78°, $[\alpha]_D -8^\circ 42'$ (Corriez, Bull. Sci. Pharmacol. 19, 468). The *platinichloride* $C_{15}H_{26}N_2 \cdot H_2PtCl_6, 2H_2O$ is yellow and decomposes at 244°–257°.

Sparteine picrate $C_{15}H_{26}N_2 \cdot 2C_6H_3O_7N_3$ has m.p. 208° (Moureu and Valeur, Compt. rend. 1903, 137, 194), 199°–200° (Wackernagel and Wolfenstein, *l.c.*).

Sparteine ferrichloride $C_{15}H_{26}N_2 \cdot 2HCl \cdot FeCl_3$ sinters at 190° (Scholtz, Arch. Pharm. 1909, 247, 534).

Sparteine ferrocyanide is a white crystalline solid, easily soluble in water (Beckurts, Arch. Pharm. 228, 347).

iso-Sparteine



has been isolated by Moureu and Valeur (Compt. rend. 1907, 145, 1184, 1343).

Numerous derivatives of sparteine and *iso*-sparteine have been prepared: for an account of these the original papers must be consulted—

Dihydrosparteine (Ahrens, Ber. 20, 2218; 21, 825).

Oxysparteine (Ahrens, Ber. 24, 1095; 25, 3607; 26, 3035; 30, 195).

Hydroxysparteine $C_{15}H_{24}ON_2$ (Ahrens, *ibid.* 1905, 38, 3268).

Dehydrosparteine (Ahrens, *ibid.* 26, 3035).

Spartyrine $C_{15}H_{24}N_2$ (Willstätter and Marx, Ber. 1905, 38, 1772).

Ethylspartyllammonium iodide $C_{15}H_{27}EtN_2I_2$ (de Coninck, Compt. rend. 104, 513).

Methyl-derivatives of *sparteine* and *iso*-sparteine (Moureu and Valeur, Compt. rend. 1905, 140, 1645; 141, 49, 117; 261, 328; 1907, 145, 815, 929, 1184; 146, 79; Moureu and Valeur, Bull. Soc. chim. 1908, [iv.] 3, 674; Compt. rend. 1908, 147, 127, 864, 1318; Valeur, Bull. Soc. chim. 1909, [iv.] 5, 31 *et seq.*; Valeur and Luce, Compt. rend. 1919, 168, 1276). V. also BROOM TOPS.

Sparteine may be estimated in tablet form by the following method: The tablets, which usually contain the sparteine in the form of a salt, are dissolved in slightly acidified water, and the alkaloid is separated by shaking the solution with two successive portions of chloroform. The solvent is evaporated on the steam bath, the final traces being removed by means of a current of air and the addition of a little ether, and the residue is cooled and weighed. The alkaloid is slightly volatile at 100°C., the loss being 3.19 p.c. after 1 hour's

and 6.6 p.c. after 7 hours' heating. Sparteine hydrosulphate may be titrated with 0.02 N-sodium hydroxide solution, with methyl red or phenolphthalein as indicator. It is not possible to titrate the separated alkaloid after extraction with chloroform, owing to the uncertain endpoint. The picric acid method is also unsatisfactory, because of the solubility of the picrate in water. Separation of the alkaloid by shaking its ethereal solution with acid and titration of the excess of acid is not practicable (P. W. Jewel, J. Amer. Pharm. Assoc. 1923, 12, 107–112; Chem. Abstr. 1923, 17, 1691).

SPATHIC IRON-ORE *v.* CHALYBITE.

SPEARMINT-OIL *v.* OILS, ESSENTIAL.

SPECIFIC GRAVITY. This term, taken strictly, means the ratio of the true weight of a given volume of a substance to the true weight of an equal volume of water at the same temperature $t^\circ\text{C.}$; the ratio is frequently indicated by the symbol d_t^t . The correction for displaced air, however, is not always made, so that the value quoted for d_t^t often means the ratio of the *apparent* weights of equal volumes of substance and water at the same temperature. The higher the specific gravity of the substance, the greater is the difference in value between the two ratios, as just defined. In the case, for example, of a liquid with a specific gravity of 1.9, the difference would amount to 1 unit in the third place of decimals.

Again, 'specific gravity' is frequently taken to mean the ratio of the true weight of a given volume of a substance at a temperature t° to the true weight of an equal volume of water at 4° : this ratio is frequently indicated by the symbol d_4^t . In view of the relation between weight and volume of water in the C.G.S. system it is evident that the specific gravity of a substance, as thus defined, has the same numerical value as its absolute density, which is the mass in grams of a cubic centimetre. It should be pointed out that the values of d_4^t recorded in the literature often refer to the ratio of the *apparent* weights of equal volumes of the substance and water at t° and 4° respectively. The indefiniteness that prevails in the use of the term 'specific gravity' makes it desirable to indicate along with each recorded value (1) whether water at t° or water at 4° is taken as the standard of reference; (2) whether a correction has been made for displaced air.

The term 'specific gravity' is used mainly in connection with the densities of liquids and solids relatively to water. Gases are usually compared with air or hydrogen as a standard, and the 'relative density' of a gas means the ratio of the weight of a given volume of the gas at given temperature and pressure to the weight of an equal volume of air (or hydrogen) under the same conditions. Owing to the uniform influence of temperature on the volumes of different gases this ratio is independent of temperature; whilst, on the other hand, the relative density or specific gravity of a liquid, d_4^t , is a variable figure.

In all determinations of specific gravity or density, the essential operation is to find the weight of a known volume of the substance at given temperature and, in the case of a gas,

given pressure. In the following sections, the chief methods used in such determinations are described.

DENSITY OF GASES AND VAPOURS.

The standard method for the accurate determination of the density of gases is the one employed originally by Regnault and perfected by later workers, notably von Jolly (Trans. Munich Acad. 1880, 13, ii. 49), Rayleigh (Proc. Roy. Soc. 1893, 53, 134), Leduc (Compt. rend. 1891, 113, 186), and Morley (Smithsonian Contributions to Knowledge, 1895; Zeitsch. physikal. Chem. 1896, 20, 68, 242). The principle of the method may be suitably explained by reference to the apparatus used by Lord Rayleigh (*l.c.*). The glass globe *s*, which can be surrounded with ice in the inverted bell-jar *t*, has about 1800 c.c. capacity and is connected with the rest of the apparatus by a short piece of thick-walled indiarubber tubing *u*. The tube *v*

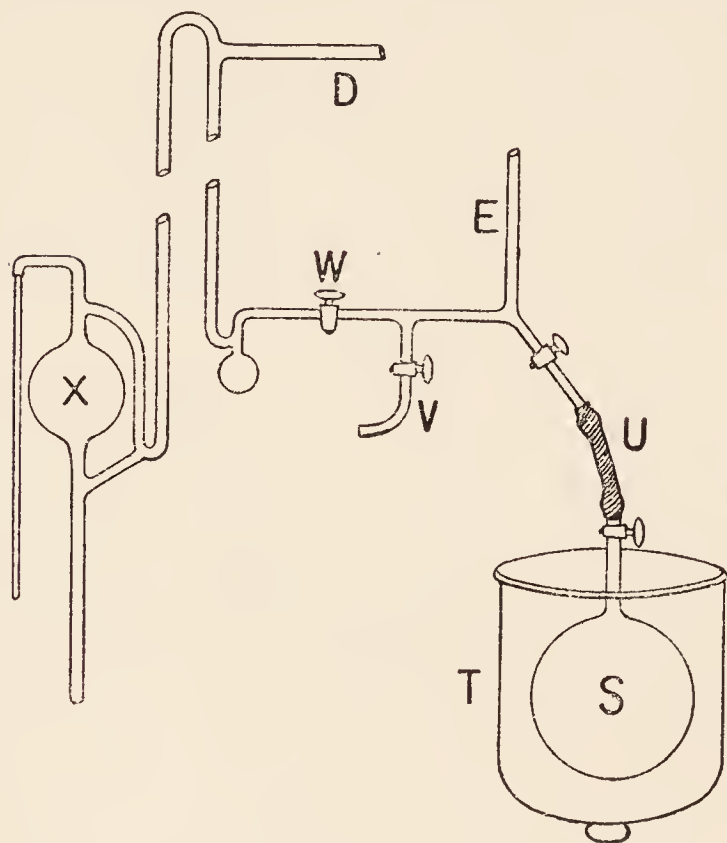


FIG. 1.

communicates with the gas-generating apparatus and connection is made through the tap *w* with a Töpler pump *x*, and further, through the tube *d*, with the vacuum chamber of a special manometer. The side tube *e* leads to the pressure chamber of the same manometer.

The volume of the globe is ascertained by finding the weight of boiled-out distilled water which it can contain up to the top of the passage in the stopcock. After it has been dried it is attached to the rest of the apparatus as shown in Fig. 1. The globe is then alternately evacuated and filled with the gas under examination, its weight being determined between each operation. During the filling of the globe it is surrounded with ice, and before the stopcock is closed the pressure is read off on the manometer. The temperature and pressure of the gas filling the globe are thus accurately known. In order to eliminate the effects of changes in the temperature and pressure of the atmosphere, and therefore in the buoyancy of the displaced air, in the interval between the weighing of the vacuous globe and the weighing of the filled globe, a

counterpoise must be employed. This should be a closed glass globe of the same external volume as the one already mentioned. The 'dummy' globe, further, should be subjected to the same treatment, in regard to washing and wiping, as the working globe, so that the two glass surfaces, when the weighing is made, shall, as far as possible, be in the same condition. In the most accurate work it is necessary to make a correction, indicated by Lord Rayleigh, for the contraction which the globe undergoes when it is evacuated. In the case of a globe of 1800 c.c. capacity, this contraction amounts to about 0.43 c.c., and the air displaced by the vacuous globe is less by this amount than the air displaced by the full globe. The weight of 0.43 c.c. of air at the temperature and pressure of the balance case must therefore be added to the observed weight of the gas filling the globe.

The foregoing method, when applied with all due precautions, gives results of high accuracy. Successive determinations by Lord Rayleigh of the weight of oxygen filling his working globe under constant conditions gave figures the extreme variation of which was about 1 part in 9000, even although the oxygen was obtained from different sources. Where the available supply of gas is small, and the use of large globes is therefore out of the question, the attainable accuracy is not so high. Travers has estimated that in the case of helium, for instance, with a globe of 30 c.c. capacity, it should be possible to determine the density to within 1 p.c. of the true value. A description of the apparatus used in finding the densities of the rare gases has been published by Ramsay and Travers (Phil. Trans. A, 1901, 197, 54). A modification of the Regnault method, applicable where the gas under examination can be condensed at the temperature of liquid air, has been described by Maass and Russell (J. Amer. Chem. Soc. 1918, 40, 1847).

The accurate determination of the densities of gases has assumed great importance in connection with certain atomic weight problems. When allowance is made for the extent to which the different gases deviate from strict adherence to Boyle's Law, that is, when the compressibility is taken into account, it is possible to deduce from the relative density of a gas found for a pressure of 760 mm. the value which it would have at an infinitely low pressure. It is then assumed that the molecular weights of different gases would be strictly proportional to such limiting densities (*see* D. Berthelot, Compt. rend. 1898, 126, 954, 1030, 1415, 1501; Rayleigh, Phil. Trans. A, 1905, 204, 351). The molecular weights so calculated were in harmony with the accepted atomic weights except in one case, viz. that of nitrogen. Here the application of the physical method of limiting densities has led to a revision of the atomic weight for this element (*see* Gray, Chem. Soc. Trans. 1905, 87, 1601; 1906, 89, 1173; Guye and others, Compt. rend. 1905, 140, 1386; 141, 826; J. Chim. phys. 1905, 3, 537; Ber. 1906, 39, 1470).

Schloesing's method for finding the relative density of a gas depends on certain well-known hydrostatic principles and can be used when only 5–10 c.c. of gas are available (*see* Compt. rend. 1898, 126, 220, 476, 896). Two long

capillary tubes, arranged vertically and communicating at the bottom through a 3-way tap, with each other or with a mercury reservoir, are charged with air, carbon dioxide and a gas X of unknown density. The carbon dioxide (supposed to be the heaviest of the three gases) occupies the lower part of the tubes, while the upper parts are occupied by air and X respectively. When equilibrium has been established between the two tubes, the positions of the two surfaces air—CO₂ and CO₂—X will obviously depend on the relative densities of air and X. These positions can be determined by allowing mercury to rise into each tube separately and drive over the contents into an absorption vessel filled with caustic potash. The unabsorbed air or X is then brought back into its tube, and the position of the mercury at atmospheric pressure is read off. In this way, without weighing and without reading the barometer, the density of X can be deduced from the densities of air and carbon dioxide.

Another method for the determination of the densities of gases was devised by Bunsen, and depends on the rate of effusion through a minute hole in a thin plate of platinum. The densities of two gases are proportional to the squares of the times of effusion, so the experiment consists in determining the time occupied by the passage of a certain volume of air through the aperture, and then determining the time required for the effusion of the same volume of the gas. The density in relation to air is obtained by dividing the square of the number of seconds recorded in the second case by the square of the number found in the first.

Bunsen's apparatus, described in his "Gasometry" (1857, 121–127), has since been improved by Schilling, and in this form is employed for controlling the density of coal gas. The results given by this apparatus are trustworthy to about 1 part in 500. The Simmance-Abady specific gravity bell is used for a similar purpose and is based on the same principle. Effusion apparatus has been employed also in the study of the rare gases (Donnan, *Phil. Mag.* 1900, 49, 423; compare Emich, *Monatsh.* 1903, 24, 747; 1905, 26, 505).

The control of the density of coal gas, already referred to, is frequently effected with the help of a so-called gas balance. The characteristic part of such an apparatus is a hollow brass sphere which takes the place of one side of the beam, and which can be filled *in situ* with the gas under examination. On the other side, the beam carries a rider and ends in a pointer which moves in front of a vertical scale (*see Lux, Zeitsch. anal. Chem.* 1887, 26, 38; 1890, 29, 13; *J. Soc. Chem. Ind.* 1890, 9, 415).

When it is desired to ascertain the density in the state of vapour of a substance which is liquid under the ordinary conditions of temperature and pressure, special methods must be adopted.

In Dumas' method of determining vapour densities, the weight of a known volume of the vapour is determined. A light glass flask, of a capacity of from 100 to 350 c.c. (according to the density of the vapour to be determined), has its neck drawn out to a fine point and bent nearly at right angles (*see Fig. 2*). The flask has to be filled with dry air, which is done by

connecting the point with a calcium chloride tube and attaching the latter to an air-pump. The flask is exhausted several times and filled with air which has passed through the drying tube. The flask full of air is now weighed, the temperature and the barometer being read simultaneously. The end of the tube is next dipped into the liquid, or into the fused substance, if the body is solid at the ordinary temperature, and by alternate heating and cooling some of the liquid is introduced into the flask. The flask is lowered into a bath of boiling water or of hot oil; the liquid boils, and its vapour expels the air. The introduction of the flask into the bath must be carried out with caution, for a dangerous pressure might be produced in the flask if the evaporation were too rapid. When the temperature of the bath is well above the boiling point of the liquid and vapour ceases to escape from the orifice, the point is sealed by a blowpipe flame, the temperature of the bath and the height of the barometer being observed at the same time. The flask is removed from the bath, cleaned, and weighed. The next process is to determine the capacity of the flask. For this purpose the point of the flask is broken under mercury, and the mercury is forced in by atmospheric pressure. If the mercury completely

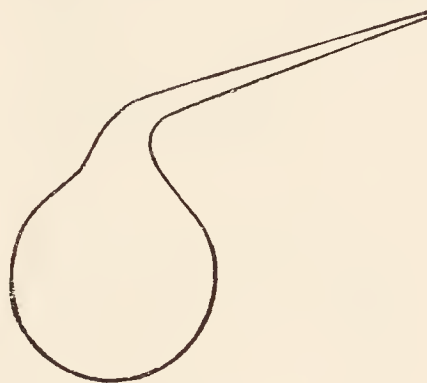


FIG. 2.

fills the flask it shows that no air was mixed with the vapour of the substance. The mercury is now poured out into a graduated vessel, and the quantity measured. This gives the volume of the vapour that the flask contained. If a bubble of air is observed above the mercury in the flask, its volume must be determined either by refilling the flask completely after measuring the mercury, or more conveniently by running mercury in from a burette until the flask is quite full of mercury with the condensed liquid above it; the volume of mercury thus introduced is equal to the volume of the residual air. The capacity of the flask is now determined by measuring the mercury as before described. The data are sufficient for the calculation of the vapour density; the weight of the flask is the weight first obtained *minus* the weight of the volume of air at the temperature and pressure at the time of weighing calculated from the volume of the flask found in the last operation. The weight of the vapour is the weight obtained in the second weighing *minus* the weight of the flask. The volume of the vapour at 0° and 760 mm. pressure is calculated from the volume of the flask and the temperature and pressure at the time of sealing, and the weight of an equal volume of air or of hydrogen is calculated from the known weights of a litre of these gases. A correction may be made for the increase of the capacity of the globe at the temperature at

which it is sealed, but in most cases this correction is unnecessary. When the Dumas method is used the substance must be pure, for if it is a mixture the portions with the lower boiling point pass off first, and the density ultimately arrived at is vitiated by the presence of the substances of higher boiling point.

The original Dumas method has been variously modified. Habermann suggested that the vaporisation in the bulb should be carried out under reduced pressure (*Annalen*, 1877, 187, 341). Less material is then required, and the bulb need not be heated beyond the ordinary boiling point of the substance. Minor modifications have been proposed by Pettersson and Ekstrand (*Ber.* 1880, 13, 1191), Pawlewski (*ibid.* 1883, 16, 1293), Schall (*ibid.* 1885, 18, 2068), Friedel and Crafts (*Compt. rend.* 1888, 106, 1764), Winkler (*Chem. Zeit.* 1899, 23, 627), Schulze (*Physikal. Zeitsch.* 1913, 14, 922). For use at very high temperatures, the bulbs may be made of porcelain instead of glass (Deville and Troost, *Ann. Chim. Phys.* 1860, 58, 257).

Instead of determining the weight of a known volume of the gasified substance it is

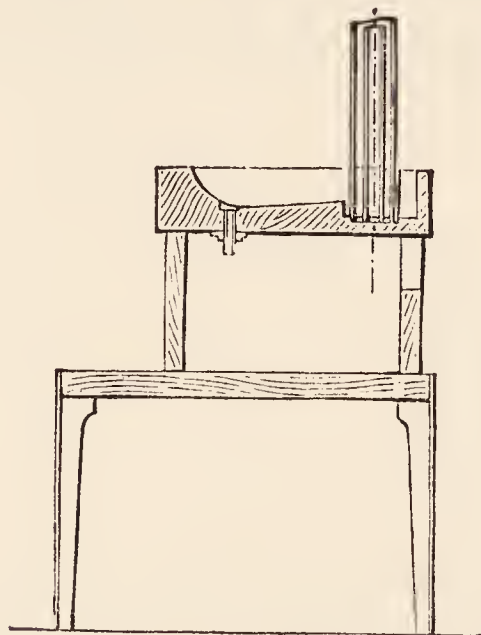


FIG. 3.—SECTION OF MERCURY TROUGH

possible to start with a known weight of the liquid, the vapour density of which is to be ascertained, and then to find the volume occupied by this in the gaseous state at known temperature and pressure. This is the principle underlying Gay-Lussac's method, in which a small sealed bulb with a known quantity of the liquid under investigation was introduced into a graduated tube filled with mercury and standing in a bath of the metal. This tube was surrounded by a cylinder containing a suitable liquid, and by heating the mercurial trough the temperature was brought to such a point that the substance in the inner tube was completely gasified. Gay-Lussac's method was notably improved by Hofmann (*Ber.* 1868, 1, 198). The graduated tube was lengthened up to a metre, so that the substance vaporised into a vacuum space and the vapour produced was under a very low pressure. This fact made it possible to ascertain the vapour density of a substance at temperatures well below its boiling point. The tube, further, was jacketed with the vapour of a boiling liquid, such as aniline or water, and the use of small stoppered bottles was suggested instead of sealed bulbs.

Hofmann's method has been applied in various modified forms (*see* Brühl, *Ber.* 1876, 9, 1368; 1879, 12, 197; Thorpe, *Chem. Soc. Trans.* 1880, 37, 147; Capstick, *Phil. Trans. A*,

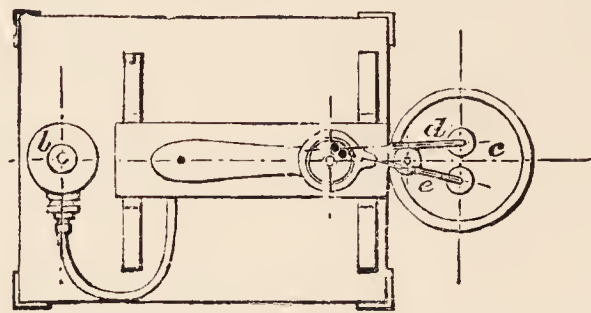


FIG. 4.—PLAN OF MERCURY TROUGH.

1894, 185, 1; Ramsay and Steele, *Phil. Mag.* 1903, 6, 492; Blackman, *Ber.* 1908, 41, 768, 4141; Magnus and Schmid, *Zeitsch. anorg. Chem.* 1921, 120, 232) and is capable of giving

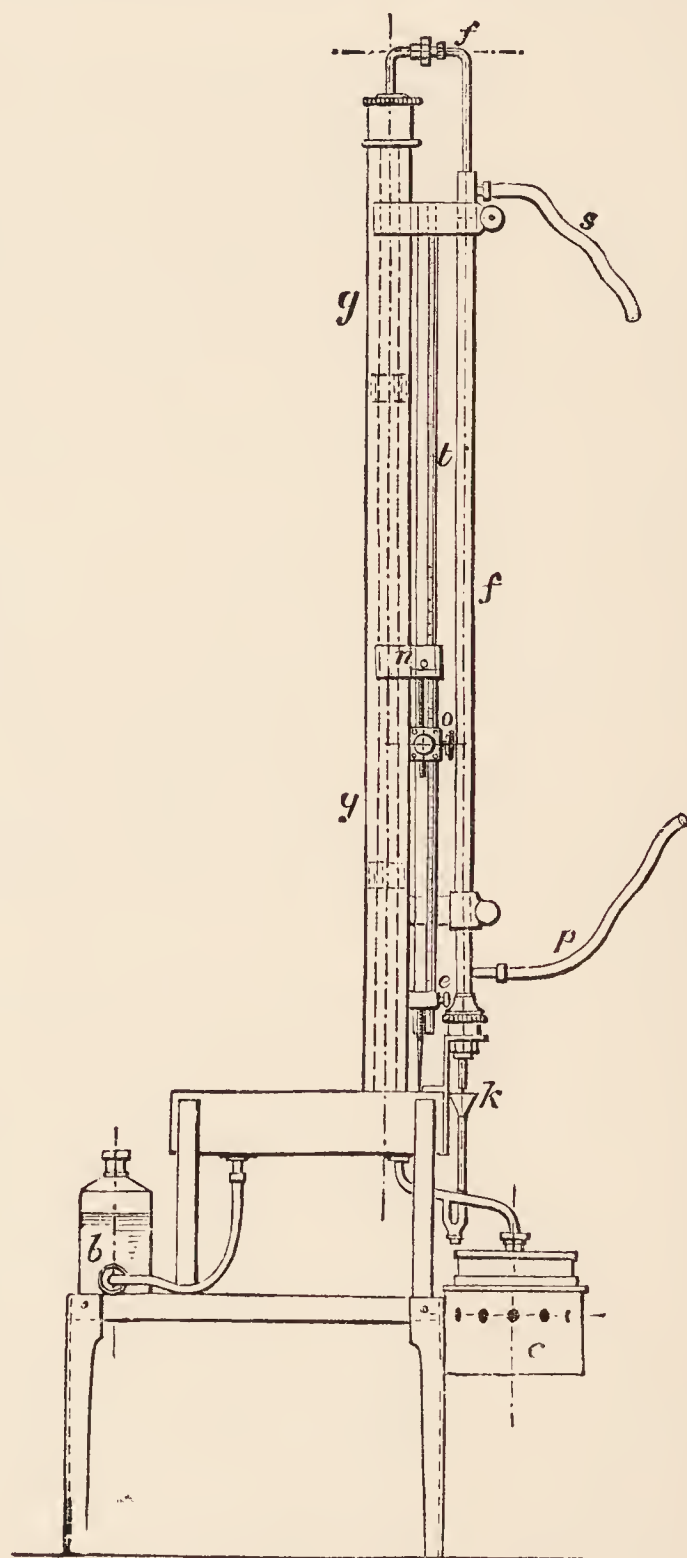


FIG. 5.

results of high accuracy. The apparatus devised by Thorpe is shown in Figs. 3-5.

Instead of the barometer tube being graduated throughout its length only one mark is

etched on it near the closed end. The capacity of the closed end to the mark is first determined, and the rest of the tube is calibrated by pouring in known quantities of mercury as in calibrating a eudiometer, the levels of the mercury in the tube being read off on a graduated scale placed by its side. The mercury trough is provided with a shallow well in which the barometer tube and the surrounding cylinder stand, and there is an opening at the bottom of the other portion of the trough by means of which the mercury may be drawn through a caoutchouc tube into a tubulated bottle. Through the bottom of the trough and into the well pass two nickel-plated copper tubes, one of which passes to the bottom and the other to the top of a copper boiler placed below the level of the trough, and containing the liquid the vapour of which is to heat the barometer tube. When an experiment is to be made the two copper tubes are connected by a short india-rubber tube (to prevent the access of mercury), and the bottle of mercury raised so as to fill the trough. The calibrated tube is next filled with mercury and inverted in the trough, and the weighed substance introduced. The tube is placed in the well, the mercury run out from the trough, and the india-rubber tube removed from the copper tubes. A wide cylinder is now placed round the barometer tube so as to inclose the tubes connected with the boiler between the cylinder and the barometer, and to the top of the wide tube a cap is fitted connected to a vertical metal condenser, which also acts as the support of the glass tubes. The liquid in the boiler is now raised to ebullition, and the vapour which condenses in the cylinder returns to the boiler by the tube which passes to the bottom, and which is a little shorter than the other tube. Any vapour which passes through the cylinder is condensed by the vertical condenser and falls into a funnel attached to the return tube to the boiler. The mercury expelled from the barometer flows over the edge of the well, and runs into the bottle. In this form of apparatus the whole of the mercury in the barometer tube is uniformly heated, which renders it possible to make an accurate correction for the pressure. When the vapour ceases to expand, the lower end of the steel scale is brought in contact with the mercury in the well, and the level of the mercury in the tube is measured by moving downwards by rack and pinion a piece of brass which partly surrounds the wide tube. This gives the height of the column in the barometer, and, by reference to the calibration table, the volume of the vapour in the tube.

A more convenient, if less accurate, process for the determination of vapour densities was devised by V. Meyer (Ber. 1878, 11, 1867, 2253). It depends on the measurement of the volume of air expelled from a closed vessel by the volatilisation of a known weight of the substance. The apparatus (see Fig. 6) consists of a cylindrical bulb, B, of about 100 c.c. capacity, attached to the end of a long tube. Near the upper end of the latter a side-tube, D, is attached which dips downwards into a water trough, and over the end of this delivery tube a graduated cylinder, H, full of water may be placed, the top of the vertical tube being closed by a cork. At the bottom of the cylindrical bulb a quantity of asbestos is placed to prevent the fracture of the

glass by the introduction of the vessel containing the substance under investigation. The bulb and part of the long tube are heated in the vapour of a liquid boiling at least 20° higher than the boiling point of the substance itself, or in a bath of molten lead. A form of outer vessel alternative to that shown in Fig. 6 has been described by Henderson (J. Amer. Chem. Soc. 1912, 34, 553). When the temperature of the inner tube becomes constant (indicated by the cessation of escape of air through the water in the trough) the graduated tube is placed over the end of the delivery tube, the cork withdrawn from the long tube, and a small vessel, containing about 0.1 gram of the substance, is allowed to fall into the apparatus and the cork immediately replaced. Instead of falling directly to the bottom of the bulb B, the small vessel may be allowed to rest on a movable rod (see Fig. 6), until the cork has been replaced. The

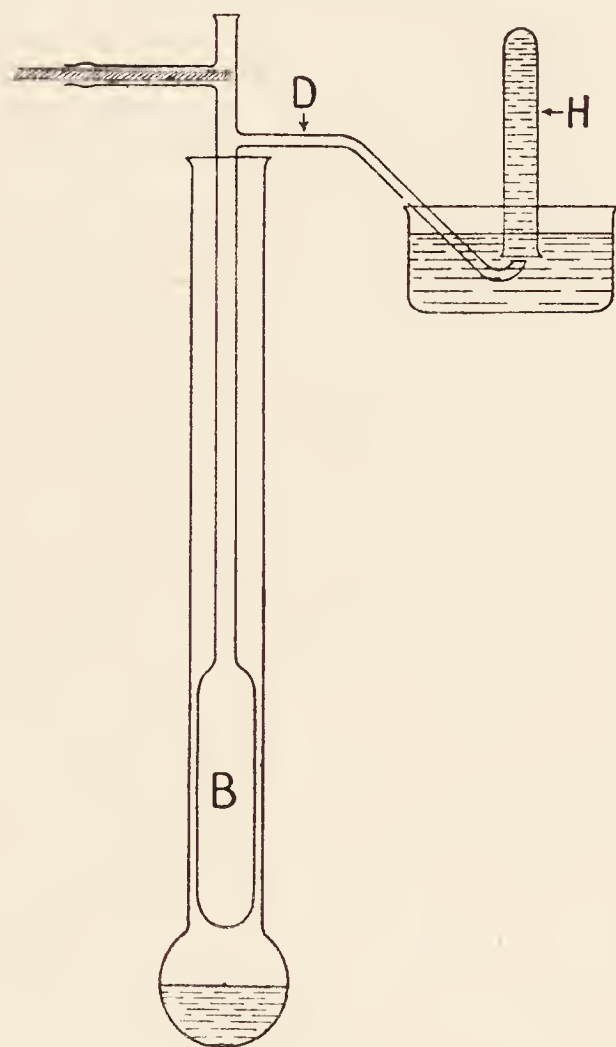


FIG. 6.

said vessel may be a small stoppered bottle or sealed bulb; in the latter case the capillary end of the bulb must be broken off before it is introduced into the apparatus. The volatile body is transformed into vapour, and air is expelled into the cylinder. The evaporation should take place so rapidly that none of the vapour (which should occupy only about the bottom third of B) diffuses into the cooler parts of the apparatus. The air expelled, when reduced to the normal temperature and pressure, is equal to the corrected volume of the vapour produced from the weighed quantity of the substance. From the data thus obtained the vapour density is calculated.

The air displaced from the apparatus may be collected and measured in a gas burette, instead of in a graduated tube over water, while the reduction to N.T.P. may be facilitated by

using a Lunge gas volumeter (Lunge and Neuberg, Ber. 1891, 24, 729). This latter apparatus has the further advantage that it permits the determination of vapour density by V. Meyer's method under reduced pressure (see also Meunier, Compt. rend. 1884, 98, 1268; La Coste, Ber. 1885, 18, 2122; Schall, *ibid.* 1887, 20, 1827, 2127; Richards, Chem. News, 1889, 59, 39; Bodländer, Ber. 1894, 27, 2267; Weiser, J. Phys. Chem. 1916, 20, 532; MacInnes and Kreiling, J. Amer. Chem. Soc. 1917, 39, 2350; Romeo, Gazz. chim. ital. 1919, 49, i. 172). Various devices have been suggested which permit the introduction of the substance into the heated space without opening the apparatus (L. Meyer, Ber. 1880, 13, 991; La Coste, *l.c.*; Bott and Macnair, Ber. 1887, 20, 916; Biltz and V. Meyer, Zeitsch. physikal. Chem. 1888, 2, 189; Eykman, Ber. 1889, 22, 2754; Patterson, Chem. News, 1908, 97, 73; Chapin, J. Ind. Eng. Chem. 1912, 4, 684).

In determining vapour density at atmospheric pressure by V. Meyer's method, the temperature of the bath should ordinarily be somewhat higher than the boiling point of the substance under examination; but Demuth and Meyer have shown (Ber. 1890, 23, 311) that if the apparatus is filled with hydrogen and provision is made for rapid diffusion and dilution of the vapour, the density may be satisfactorily determined at temperatures below the boiling point. If it is desired to find vapour densities at very high temperatures the apparatus must be made of some refractory material, such as platinum, porcelain or iridium (see V. and C. Meyer, Ber. 1879, 12, 1112; V. Meyer, *ibid.* 1880, 13, 394; Crafts, Compt. rend. 1880, 90, 183; Nilson and Pettersson, J. pr. Chem. 1886, 33, 1; Zeitsch. physikal. Chem. 1889, 4, 211; Biltz and Meyer, *ibid.* 1889, 4, 249; Biltz, *ibid.* 1896, 19, 385; Meyer and Recklinghausen, Ber. 1897, 30, 1926). For vapour density determinations in the neighbourhood of 2000°, Nernst uses a small iridium vessel, coated with magnesia and asbestos, in which 0.1–1.0 mg. of the substance under investigation is vaporised. The substance is weighed on a special micro-balance and the increase of volume due to vaporisation is measured by the displacement of a thread of mercury in a calibrated capillary tube (see Zeitsch. Elektrochem. 1903, 9, 622; also Löwenstein, Zeitsch. physikal. Chem. 1906, 54, 707; von Wartenberg, Zeitsch. anorg. Chem. 1907, 56, 320).

It is one of the advantages of V. Meyer's displacement method that the temperature at which vaporisation takes place need not be known. In certain cases, however, notably those in which the vapour density varies with temperature, it is desirable to know the temperature of vaporisation. This can readily be ascertained either by using the vapour density bulb itself as an air thermometer (Nilson and Pettersson, J. pr. Chem. 1886, 33, 1; Biltz and Meyer, Zeitsch. physikal. Chem. 1889, 4, 249), or by sweeping out and measuring the volume of some readily absorbed gas, such as carbon dioxide or hydrogen chloride, which fills the bulb at the temperature of observation (see Crafts and Meier, Compt. rend. 1880, 90, 606; Meyer and Züblin, Ber. 1880, 13, 2021; Mensching and Meyer, Zeitsch. physikal. Chem.

1887, 1, 145). In both these methods the uncertainty arising from the unequal temperature of the stem of the vapour density bulb is eliminated by the use of a 'compensator,' a blind tube of the same dimensions as the stem. The compensator is exposed to the same conditions as the stem, and the gas it gives up or contains is deducted from the corresponding volume for the stem + bulb.

As has been already pointed out, the vapour density of a substance may be deduced from the increase in volume due to the vaporisation of a known weight at constant pressure. It is equally possible to deduce the vapour density from the increase of pressure due to the vaporisation of a known weight at constant volume.

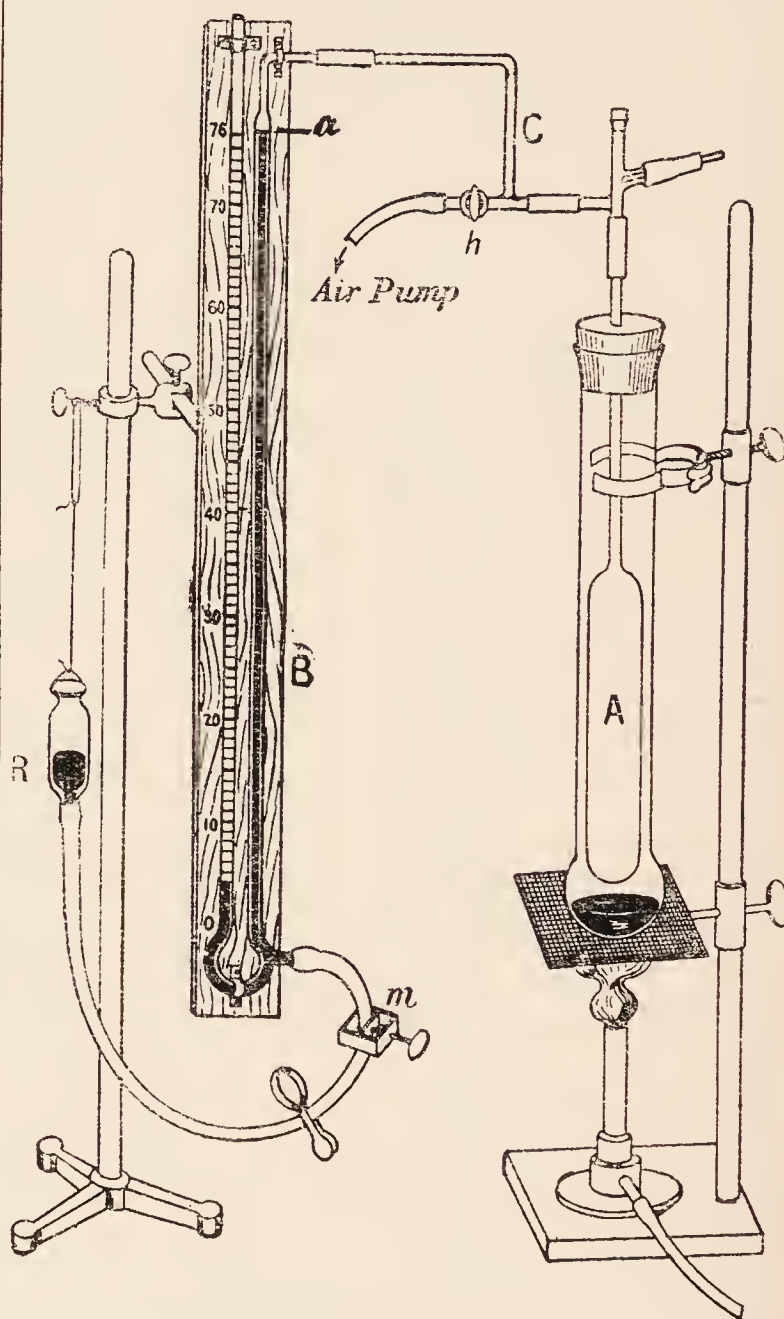


FIG. 7.

Such a method of finding vapour density is based on the principle that equimolecular quantities of different substances, vaporised in a given space and at a given temperature, produce the same increase of pressure. Many forms of apparatus, based on this principle, some of them adapted for working under reduced pressure, have been proposed (Pfaundler, Ber. 1879, 12, 165; Dyson, Chem. News, 1886, 55, 88; Bott and Macnair, Ber. 1887, 20, 916; Schall, Ber. 1887, 20, 1435, 1759; 1888, 21, 100; 1889, 22, 140; 1890, 23, 919, 1701; Malfatti and Schoop, Zeitsch. physikal. Chem. 1887, 1, 159; Eykman, Ber. 1889, 22, 2754; Richards, Chem. News, 1889, 59, 87; Bleier and Kohn, Monatsh. 1899, 20, 505; Erdmann,

Zeitsch. anorg. Chem. 1902, 32, 425; Lumsden, Chem. Soc. Trans. 1903, 83, 342; Haupt, Zeitsch. physikal. Chem. 1904, 48, 713; Blackman, Chem. News, 1909, 100, 13, 174). Fig. 7 shows the apparatus used by Bleier and Kohn. The vaporisation bulb A is connected with a manometer, B, and, through the stopcock *h*, with a pump. By adjusting the height of the reservoir R, the mercury in the right-hand limb of the manometer is brought to the same level *a* before and after vaporisation; the change of pressure due to vaporisation is read off on the left-hand limb. The fine adjustment of the mercury at *a* is effected by the screw clip *m*.

Reference may be made here to Gibson's method of finding vapour densities at high temperatures (Proc. Roy. Soc. Edin. 1913, 33, 1), which depends on the measurement, with a quartz manometer, of the pressure produced by the volatilisation of a known quantity of material in a known volume.

A simple comparative method for determining vapour densities has been devised by Blackman (Chem. Soc. Trans. 1915, 107, 1500).

DENSITY OF LIQUIDS.

One common way of finding the density of a liquid is to determine the mass of the liquid which exactly fills a vessel of known volume. The vessels usually employed for this purpose are known as specific gravity bottles and pycnometers. The simplest form of specific



FIG. 8.

gravity bottle is a thin glass flask with a flat bottom and an accurately-fitting stopper, through which a fine hole is drilled (see Fig. 8). The dry, clean flask is carefully weighed and then filled with the liquid, the temperature being noted. The stopper is then placed in the neck, the excess of liquid escapes through the perforation in the stopper and is wiped off from the glass, and the flask

is again weighed. The flask is now emptied, cleaned, filled with distilled water, and again weighed. If the temperature of the water is the same as that of the liquid at the moment of putting in the stopper, then the weight of the liquid (*w*) divided by the weight of the water (*w'*) gives the relative density of the liquid to that of water at the particular temperature *t*°. If the absolute density is required, a correction must be made (1) for the quantity of air displaced by the liquids and the weights, (2) for the deviation of the density of the water from unity. If *D* is the absolute density

of the liquid at *t*°, then $D = \frac{w}{w'} \Delta + \sigma \left(1 - \frac{w}{w'}\right)$,

where Δ is the density of water at *t*°, and σ is the density of the air at the time of the observations. In most cases it is sufficient to take $\sigma = 0.0012$, and a table may therefore be constructed giving the values of the correction term

$\sigma \left(1 - \frac{w}{w'}\right)$ for various values of the uncorrected

density $\frac{w}{w'}$. (For a discussion of these corrections, see Wright, J. Soc. Chem. Ind. 1892, 11,

297; Wade and Merriman, Chem. Soc. Trans. 1909, 95, 2174; Hartley and Barrett, *ibid.* 1911, 99, 1073; Barr, *ibid.* 1924, 125, 1040.)

The special form of bottle just described is not free from objection, for evaporation takes place at the top of the perforated stopper, and further, if the temperature of the balance case is higher than the temperature at which the bottle was filled, there is an overflow. The first difficulty may be avoided by having a cap ground to fit the neck of the bottle (Louis, J. Soc. Chem. Ind. 1894, 13, 322). The second difficulty may be met by grinding into the neck of the flask a tube which is contracted in its middle to a capillary bore, and is provided at the top with

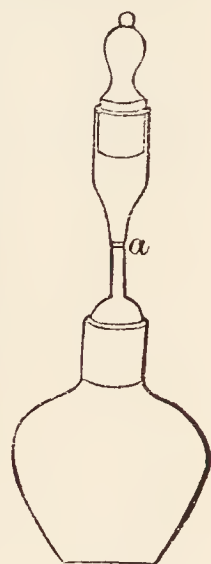


FIG. 9.

a small reservoir closed by a stopper (Fig. 9). To use this modification, the flask is filled and the tube inserted. This forces a small quantity of the liquid through the capillary tube into the reservoir above. The flask is now placed in a bath of known temperature, or even in water at 4°, and left there until its temperature is constant. If the liquid contracts so as to empty the reservoir above the capillary tube, a small additional quantity is introduced. When no change of volume is perceptible, a thin piece of filter paper or a fine glass tube is introduced into the reservoir so as to reduce the level of the liquid to a mark, *a*, which is made on the outside of the capillary tube. The stopper may then be introduced into the reservoir, the flask removed from the bath and its outside dried, and it may now be left until it has reached the temperature of the balance case where it is to be weighed.

Various modifications of this form of specific gravity bottle have been suggested (see Squibb, J. Amer. Chem. Soc. 1897, 19, 111; Leimbach, J. pr. Chem. 1902, 66, 475; Bošnjaković, Zeitsch. anal. Chem. 1904, 43, 230). It has been proposed, too, that the capillary tube should be provided not with a single mark, but with regular graduations, the values of which are determined once for all (Tribe, Chem. News, 1873, 28, 211; Squibb, J. Amer. Chem. Soc. 1897, 19, 111; see also Louis, J. Soc. Chem. Ind. 1894, 13, 322).

The Sprengel pycnometer (Chem. Soc. Trans. 1873, 26, 577) is a U-shaped tube terminating in two capillary tubes bent in opposite directions (Fig. 10). The liquid is aspirated into the tube, which is then sunk in a beaker of water at known temperature, the capillary tubes resting on the edges. When the temperature of the liquid is constant, as shown by the cessation of movement of the liquid in the capillary tube, some of the liquid is removed from one capillary, which terminates in a fine point, *a*, by means of a piece of filter paper, until the liquid in the other capillary reaches a mark, *b*, near the bend. Should the amount of liquid in the pycnometer be insufficient a little is conveniently added by touching the point *a* with a drop held on the end of a glass rod. Sprengel's pycnometer was modified by Ostwald (J. pr. Chem. 1877, 16, 396), who made the limb of the U-tube next to *b* of narrow-bore tube

throughout. In the case of volatile or hygroscopic liquids, it is advisable to close the ends of the capillaries, after the adjustment has been made, with glass caps.

Immediate contact of the liquid with the air is avoided, and determination of the density at temperatures below that of the laboratory is made possible by Perkin's modification of the Sprengel pyknometer (Chem. Soc. Trans. 1884, 45, 443; 1896, 69, 1043). In this the narrow

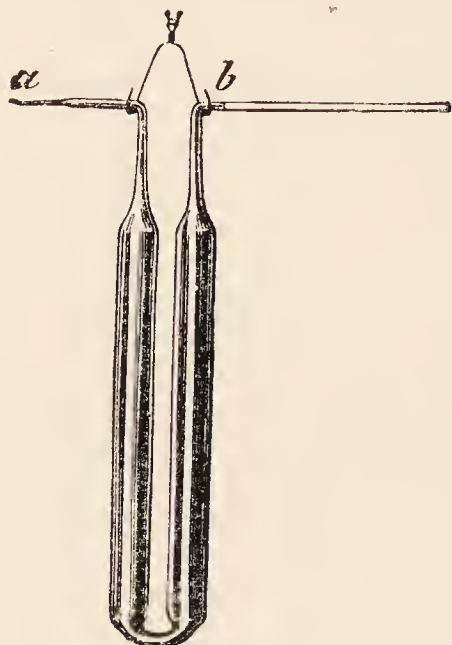


FIG. 10.

tubes are bent at obtuse angles instead of right angles, and a small bulb is blown on the tube adjoining the shorter limb (see Fig. 11). A mark, *a*, is made just below the small bulb, the other limb terminating in a fine opening at *b*. After the liquid has been introduced into the tube, the latter is immersed in a beaker of water until the temperature of the liquid is constant. The tube is then tilted, and a piece of filter

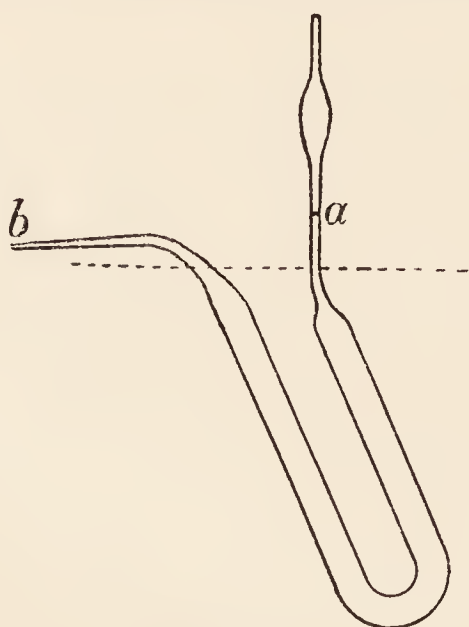


FIG. 11.

paper is placed in contact with the point *b* until the liquid in the other limb falls to the mark *a*; the filter paper is withdrawn, and the tube restored to the vertical position. The liquid recedes from the end *b* of the tube and rises in the other limb, and if the temperature becomes higher before weighing, the small bulb offers sufficient space to contain the liquid and thus prevent overflowing.

An improved form of Sprengel pyknometer has been described by Davis and Pratt (J. Amer. Chem. Soc. 1915, 37, 1199). It consists of a single closed tube of thin glass of the

desired capacity, into the top of which are fused two capillary tubes. One of these, which is attached centrally, is bent a little above its point of emergence to an angle of 60°, and drawn out slightly at the end. This capillary is continued axially inside the reservoir in the form of a tapered thin glass tube reaching almost to the bottom, and having a bore at the lower end approximately equal to the capillary bore. The other capillary, attached slightly towards the side of the reservoir, is bent at a right angle, its bore in the vertical portion being enlarged into a small bulb sufficient to accommodate the expansion of the liquid over a rise in temperature of 10°C. A mark is etched on this capillary just below the taper of the bulb. The apparatus has the appearance of a tubular wash-bottle. In adjusting the instrument when filled, a rubber tube is attached to the right-angled capillary, and the liquid blown

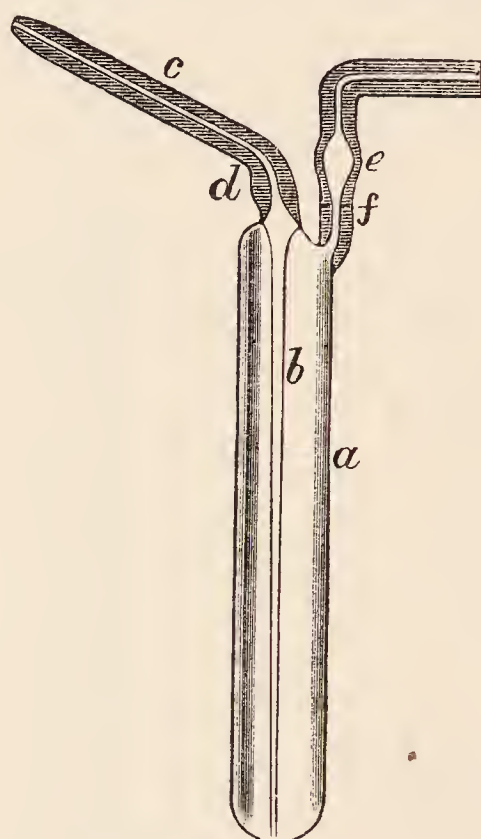


FIG. 12.

gently out of the other until its level corresponds with the mark. The point is wiped with filter paper, and, on removing the pressure, the liquid falls back in the inclined capillary, thereby reducing the danger of evaporation or accidental loss after adjustment. The advantages of this form of pyknometer are minimum weight, minimum length and projection of capillary arms, ease of cleaning and drying (Analyst, 1915, 420).

Various other modifications of the pyknometer have been suggested (Minozzi, Gazz. chim. ital. 1899, 29, i. 406; Leimbach, J. pr. Chem. 1902, 66, 475; Fischer, Chem. Zeit. 1904, 28, 359; Stanford, Phil. Mag. 1905, 10, 269; Bousfield, Chem. Soc. Trans. 1908, 93, 679; Hartley and Barrett, *ibid.* 1911, 99, 1072; Bousfield, *ibid.* 1915, 107, 1405).

Tables and formulæ for calculating specific gravities from one temperature to another are given by Saar (Chem. Zeit. 1922, 46, 433).

In chemical technology the densities of liquids are most usually determined by means of the hydrometer. This instrument is based on the fact that when a solid floats in a liquid, the weight of the liquid displaced is equal

to the weight of the floating body. The general form of the hydrometer is a spherical or cylindrical glass bulb, with a narrow stem, and the bulb is weighted at the bottom so that the instrument floats vertically in the liquid (Fig. 13).

When the hydrometer is placed in a liquid, it sinks until it has displaced a quantity of liquid equal to the weight of the instrument; it then floats in a position of equilibrium. If placed in a liquid of higher density it will not sink so deep, for the volume of this latter liquid possessing the same weight as the hydrometer will be

smaller than in the first case. Again, when placed in a liquid of lower density, it will sink deeper, for a larger volume has to be displaced before the weight of the hydrometer is supported. The density of the liquid is found by readings of the graduations marked on the stem. The stem may be divided to give densities directly, but then the divisions are not of equal length, the differences of length being proportional to the differences of the reciprocals of the densities. Hydrometers, however, are frequently graduated with divisions of equal length, tables being employed to convert the readings into densities if desired. In any case, it should be borne in mind that a hydrometer is a comparatively rough apparatus, and too much reliance should not be placed on the readings of any particular instrument, until its scale has been checked at one or two points.

In technical work, hydrometers indicating the specific gravity directly are often used for liquids lighter than water, but almost never in the case of liquids heavier than water. Twaddell's hydrometer, commonly used in Great Britain, is graduated on the same principle as those giving the specific gravity directly, but the readings on the scale are in degrees, each one of

which corresponds to a difference of 0.005 in the specific gravity. The zero of the scale is at the point to which the hydrometer sinks in water, so that a reading of 9°Tw., for example, corresponds to a gravity $1.000 + 0.005 \times 9 = 1.045$, and one of 53°Tw. corresponds to the gravity 1.265. To cover the range of specific gravity 1.00–1.85, a set of six instruments is generally supplied. An instrument based on the same principle as Twaddell's hydrometer is the densimeter described by Fleischer (Dingl. poly. J. 1876, 222, 159).

The chief hydrometer with a scale graduated in divisions of equal length is Baumé's, commonly used on the Continent and in the United States. The scale was fixed according to Baumé's original directions in the following manner. For liquids denser than water, 15 parts of pure sodium chloride are dissolved in 85 parts of water at a temperature of 10° Réaumur (12.5°C. or 54.5°F.). The zero of the instrument is the point to which the hydrometer sinks in distilled water, and the point to which it sinks in the

15 p.c. solution of salt is marked 15. The distance between the zero and this point is divided into 15 equal parts, and the whole stem graduated with similar divisions. For liquids lighter than water the zero of the hydrometer is fixed by a 10 p.c. solution of sodium chloride, distilled water giving the division 10. This instrument is, of course, graduated in the opposite direction, the zero being at the bottom of the scale.

Much confusion and irregularity, however, arose in connection with the interpretation of the Baumé degree (*see* Gerlach, Dingl. poly. J. 1870, 198, 315; Chandler, Acad. Nat. Sciences, Philadelphia, 1881). Recently the practice has been to mark the hydrometer 66°B. at the point to which it sinks in 'English sulphuric acid' (93–95 p.c. H_2SO_4) at 17.5°C., and to divide the interval between this and 0° into 66 equal parts. Obviously, this definition of the Baumé degree is not satisfactory, and accordingly attempts have been made to construct a 'rational' Baumé hydrometer. If one of these instruments sinks to 0° in water and to n° in a liquid of specific gravity d , it is easy to show that

$\frac{nd}{d-1} = C$, a constant. If now for $d = 1.842$, n is taken as 66° at 15°C., then $C = 144.3$ and hence $d = \frac{144.3}{144.3 - n}$ (*see* Fuchs, Zeitsch. anal. Chem. 1899, 38, 333).

The Baumé hydrometer with a scale based on this formula is commonly used in Germany, but elsewhere other formulæ are employed for the evaluation of the degree. Thus, in

Holland, the formula $d = \frac{144}{144 - n}$ is taken as the basis of the Baumé scale, in the United States

the formula $d = \frac{145}{145 - n}$ (*see* Emery, J. Amer. Chem. Soc. 1899, 21, 119). If Gerlach's determination (*l.c.*) of the specific gravity of a 10 p.c. salt solution at 15°C. is taken as a basis, the resulting formula is $d = \frac{146.3}{146.3 - n}$.

The Baumé hydrometer for liquids lighter than water is graduated in two ways, the relation between degrees and gravity being given

by the formula $d = \frac{146}{136 + n}$, or the American

formula $d = \frac{140}{130 + n}$ (*see* Emery, J. Amer. Chem. Soc. 1899, 21, 119).

The following table gives the values of the specific gravity corresponding to the readings of this instrument:—

Degrees Baumé	$d = \frac{140}{130 + n}$ at 60°F.	$d = \frac{146}{136 + n}$ at 12.5°C.	Degrees Baumé	$d = \frac{140}{130 + n}$ at 60°F.	$d = \frac{146}{136 + n}$ at 12.5°C.
10	1.000	1.000	36	0.843	0.849
12	0.986	0.987	38	0.833	0.839
14	0.972	0.973	40	0.824	0.830
16	0.959	0.961	42	0.814	0.820
18	0.946	0.948	44	0.805	0.811
20	0.933	0.936	46	0.796	0.802
22	0.921	0.924	48	0.787	0.794
24	0.909	0.913	50	0.778	0.785
26	0.897	0.901	52	0.769	0.777
28	0.886	0.890	54	0.761	0.768
30	0.875	0.880	56	0.753	0.760
32	0.864	0.869	58	0.745	0.753
34	0.854	0.859	60	0.737	0.745



FIG. 13.

In the following table are recorded the specific gravities corresponding to readings of the Baumé instrument for liquids denser than water, deduced (1) from the formula $d = \frac{144.3}{144.3 - n}$,
(2) from the formula $d = \frac{145}{145 - n}$.

De- grees <i>n</i>	$d = \frac{144.3}{144.3 - n}$ at 15°C.	$d = \frac{145}{145 - n}$ at 60°F.	De- grees <i>n</i>	$d = \frac{144.3}{144.3 - n}$ at 15°C.	$d = \frac{145}{145 - n}$ at 60°F.
1	1.007	1.007	34	1.308	1.306
2	1.014	1.014	35	1.320	1.318
3	1.022	1.021	36	1.332	1.330
4	1.029	1.028	37	1.345	1.343
5	1.037	1.036	38	1.357	1.355
6	1.045	1.043	39	1.370	1.368
7	1.052	1.051	40	1.383	1.381
8	1.060	1.058	41	1.397	1.394
9	1.067	1.066	42	1.410	1.408
10	1.075	1.074	43	1.424	1.422
11	1.083	1.082	44	1.438	1.436
12	1.091	1.090	45	1.453	1.450
13	1.100	1.099	46	1.468	1.465
14	1.108	1.107	47	1.483	1.480
15	1.116	1.115	48	1.498	1.495
16	1.125	1.124	49	1.514	1.510
17	1.134	1.133	50	1.530	1.526
18	1.142	1.142	51	1.547	1.543
19	1.152	1.151	52	1.563	1.559
20	1.162	1.160	53	1.580	1.576
21	1.171	1.169	54	1.597	1.593
22	1.180	1.179	55	1.615	1.611
23	1.190	1.189	56	1.634	1.629
24	1.200	1.198	57	1.652	1.648
25	1.210	1.208	58	1.671	1.667
26	1.220	1.219	59	1.691	1.686
27	1.231	1.229	60	1.711	1.706
28	1.241	1.239	61	1.732	1.726
29	1.252	1.250	62	1.753	1.747
30	1.263	1.261	63	1.774	1.768
31	1.274	1.272	64	1.796	1.790
32	1.285	1.283	65	1.819	1.813
33	1.297	1.295	66	1.842	1.835

Other hydrometers designed for liquids lighter than water are occasionally used. In Cartier's hydrometer 21° corresponds with 21°B., but above and below this point 15 degrees Cartier=16 degrees Baumé. In Beck's hydrometer the zero corresponds with $d=1.000$ and 30° with $d=0.850$: the thirtieth of this interval is 1° and equal divisions are continued in both directions as far as desired.

In addition to the general hydrometers just mentioned there are also a number of instruments used for certain special purposes, such as Sikes' hydrometer and Tralles' alcoholometer for ascertaining the strength of spirits (*see* ALCOHOLOMETRY), and various saccharometers for finding the specific gravity of saccharine solutions (*see* SUGAR).

All the foregoing hydrometers are instruments of variable immersion.

Nicholson's hydrometer, on the other hand, is a constant immersion instrument, and consists of a cylindrical metallic bulb connected at the bottom by a wire to a cup, and also an inverted cup pierced with holes. The top of the float is connected by a wire to a pan, on which weights may be placed. This wire has a single mark on it, which is brought to the surface of the liquid by weights placed on the upper scale

pan. The instrument is so adjusted that when floating in distilled water at 62°F., 1000 grs. placed on the scale pan will bring the mark on the stem to the surface of the water. When placed in a denser liquid, more weights have to be added to the 1000 grs. in order to bring the mark to the level of the liquid, and as the same volume of liquid is displaced as in the case of the water, the weights at once give the density of the liquid referred to that of water at 62°F. The cups below the float are used in the determination of the densities of solids, and will be referred to subsequently.

Another somewhat similar hydrometer consists of a cylindrical glass weight suspended from the arm of a balance, and is so counterpoised that the balance is in equilibrium when the plunger is sunk in distilled water. This is the principle of the Mohr-Westphal balance (Fig. 14). When placed in liquids of other densities the weights have to be altered to bring the balance to equilibrium, and the weights, which are generally used in the form of riders, are so arranged that the density of the liquid is read off directly. A thermometer may be placed within the glass plunger with its bulb projecting below, so that the temperature of the liquid can be determined simultaneously.

For the effect of variation in weight of the riders and plummets of the Westphal balance on the accuracy of specific gravity determinations, *see* Tschudy, J. Amer. Chem. Soc. 1922, 44, 2130. Accurate specific gravity determinations with the Westphal balance are possible only when the weight of water displaced by the plummet at 15° and the weights of the riders have an exact multiple relationship among themselves. Variations in weight of the riders which disturb this relationship produce errors, often of considerable magnitude, in specific gravity determinations.

Inaccurate plummet thermometers are also a source of error. The paper just mentioned shows how the magnitude of ordinary variation in weight of riders and plummet can be found and equations are derived for computing the correction which must be applied to any indicated balance reading in order to obtain the true specific gravity of liquids, lighter or heavier than water.

In finding the density of fused metals a quartz flask has been used as sinker (Pascal and Jouniaux, Compt. rend. 1914, 158, 414).

The submerged sinker method has been

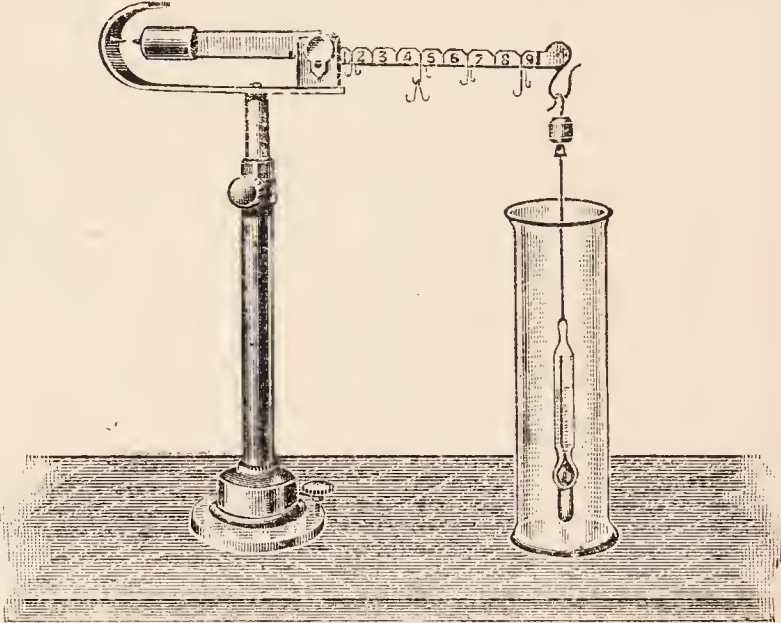


FIG. 14.

pecially developed by Lamb and Lee (*J. Amer. Chem. Soc.* 1913, 35, 1666) for the very accurate determination of the density of dilute aqueous solutions. The sinker employed was an inverted flask of about 250 cub. cm. capacity, weighted with mercury and containing a fixed vertical soft iron rod, so that the flask could be moved up and down by electromagnetic means. Platinum weights are placed on the sinker until it just floats, and the electromagnet is then regulated so that the sinker is pulled down until a platinum point, fused into the sealed neck of the flask, just touches a platinum saucer at the bottom of the vessel. The current in the electromagnet having been previously calibrated in terms of weight, the density of the liquid can be deduced. It is claimed that the figures obtained are accurate to one unit in the seventh decimal place.

C. W. Foulk has described a precision hydrometer. The principle is that of a submerged floating equilibrium with a chain hung in a catenary curve between the float and an independent point of support. The float can move freely along a tube which is open at both ends and has a suitable scale marked on it. The advantages of such an arrangement are: (1) greatly increased sensitiveness of the float to changes in density of the liquid; (2) changes in density of the liquid, however small, cause proportional changes in the position of the float; (3) the catenary hanging of the chain prevents tangling; (4) the apparatus is easily handled. The effect of the various constants of such a balanced float on its response to differences of density of the liquid is given with close approximation by the equation

$$\Delta d = \frac{(D-d) \times \Delta b}{2D \times V} \times w$$

where Δd = density change in liquid which causes a vertical displacement of float of Δb , measured in cm.; D = density of the material of the chain; d = density of liquid; V = volume of float measured in c.c.; and w = weight in grammes of 1 cm. of chain. It will be seen that the sensitiveness of the instrument is proportional to the volume of the float and inversely proportional to the weight of unit length of chain. The author describes various modifications of the instrument (*Foulk, Optical Soc. of America, J. and Rev. Sci. Inst.* 1923, 7, 327-334).

Another method of determining the densities of liquids depends on the fact that if columns of two liquids of different densities are made to support one another, the lengths of the columns will be inversely as the densities. An inverted glass U-tube with the limbs graduated upwards from 0 near the open ends is employed; at the bend of the tube there is attached a tubulure closed by a stopcock, or by a piece of caoutchouc tube with screw-clip. One of the open ends of the tube is placed in water, and the other into the liquid of which the density is sought, and suction is applied. The liquids rise in the tubes, and after adjusting the outside levels to the zero marks, the lengths of the columns are read off. In order to avoid capillarity effects the tubes should be not less than 6 mm. internal diameter. Various forms of apparatus based on this principle have been described (*Hare, Silliman's J.* 1826, 11, 133; *Alexander, Ann. Chim. Phys.*

1847, 70, 137; *Tate, Phil. Mag.* 1859, 17, 254; *Schiff, Annalen*, 1862, 121, 82; *Weber, Beiblätter*, 1879, 3, 770; *Girardet, Bull. Soc. chim.* 1901, 25, 936; see also *Watson's Practical Physics*, 29; compare *Lefebvre, Chem. Zentr.* 1897, ii. 402).

For some purposes the density of a liquid has to be determined at its own boiling point. This may be done by suspending a specific gravity flask filled with the liquid in another vessel containing some of the same liquid, which is raised to the boiling point. This heats the contents of the flask, and when the liquid ceases to expand the stopper is placed in the bottle, which is then removed from the vessel, allowed to cool, and weighed (*C. Schall, Ber.* 1884, 17, 2201). A pyknometer of the shape shown in *Fig. 15* (*Neubeck, Zeitsch. physikal. Chem.* 1887, 1, 652) may be conveniently used instead of a specific gravity bottle. Another instrument employed in finding densities at high temperatures is the dilatometer, which is a kind of thermometer with a graduated tube, the capacity of the tube and bulb being accurately known. The density of the liquid is first determined by the ordinary specific gravity bottle, and then some of the liquid is introduced into the dilatometer, the temperature of which is gradually raised, and the increase of volume measured. When the coefficient of expansion has been thus determined, the density at any temperature may be calculated. For a complete account of the methods of using dilatometers, and all the precautions necessary in their manipulation, see *Thorpe (Chem. Soc. Trans.* 1880, 37, 155; 1893, 63, 262).

For the determination of critical densities and of the densities of liquids in contact with saturated vapour at temperatures up to the critical temperature, special methods are employed (see *Ramsay and Young, Phil. Trans. A*, 1886, 177, 123; 1887, 178, 57, 313; 1889, 180, 137; *Young, Chem. Soc. Trans.* 1889, 55, 486; 1891, 59, 37, 125, 911; *Proc. Phys. Soc.* 1895, 13, 617; *Phil. Mag.* 1900, 50, 291; *Amagat, Compt. rend.* 1892, 114, 1093; *Young and Thomas, Chem. Soc. Trans.* 1893, 63, 1199; *Centnerszwer, Zeitsch. physikal. Chem.* 1904, 49, 199).

The procedure involved in the determination of the density of liquids at low temperatures has been described by *Archibald and Ure* in their study of acetone down to -90° (*Chem. Soc. Trans.* 1924, 125, 726).

DENSITY OF SOLIDS.

In determining the density of a solid it is necessary to find its mass, and also the mass of an equal volume of water, or, what comes to the same thing, to find the volume of the solid, from which the mass of the water can be calculated. In some few cases this may be done by measurement, as, for example, the measurement of a cubic foot of a body, like stone, which may be cut into a regular shape. It more generally happens, however, that the solid is irregular in shape, or is even in the form of powder: other methods must then be adopted.

One of the simplest methods is to place some water or other liquid of known density in a



FIG. 15.

graduated tube and measure it, and then introduce a weighed quantity of the solid, and observe the rise of level of the liquid in the tube. Or the tube may be weighed before and after the introduction of the solid, the increase of weight giving the quantity of the solid introduced (Schiff, *Annalen*, 1858, 107, 59; Osann, *Ann. Phys. Chem.* 1859, 106, 334; Dobbie and Hutcheson, *Phil. Mag.* 1884, 17, 459; Erdmenger and Mann, *Chem. Zeit.* 1893, Suppl. 289; Stanger and Blount, *J. Soc. Chem. Ind.* 1894, 13, 456; McKenna, *J. Amer. Chem. Soc.* 1899, 21, 50; Jacobsen, *Bull. Soc. chim. Belg.* 1904, 18, 198; von Wrochem, *Chem. Zentr.* 1905, i. 1577). Gentilé (*J. Pharm.* 1867, [iv.] 5, 401) uses a small bottle with a bulb at the top of 1 c.c. capacity. The bulb is connected to the bottle by a narrow tube with a mark on it, and there is another mark on a similar tube above the bulb. The bottle is filled with liquid to the lower mark and weighed; the solid is introduced until the liquid reaches the upper mark, and the whole is again weighed. This increase of weight is that of 1 c.c. of the solid.

A similar process, which may be employed when the solid is in small fragments or in powder, is to fill a specific gravity bottle with water, and counterpoise it on a balance. Some of the solid is then placed on the pan of the balance and weighed; the solid is now placed in the specific gravity bottle, and the level of the water adjusted. On again weighing, the quantity will be found to be less than the previous amount, the difference being due to the quantity of water expelled by the introduction of the solid, this water, of course, occupying the same volume as the solid. The density of the solid relative to water at the same temperature is at once found by dividing the weight of the solid by the weight of the quantity of water expelled. Some precautions are necessary in this method. Many solids, especially in the form of powder, entangle a quantity of air, which replaces some of the water in the bottle, or may even cause some of the solid to float in the liquid. This air may be removed by placing the specific gravity bottle containing the water and the solid in an air-pump receiver; the diminution of pressure causes the entangled air to expand and escape from the surface of the water (for a "vacuum pyknometer," see Washburn and Navias, *J. Amer. Ceramic Soc.* 1922, 3, 565). For a solid the density of which alters with time, a dilatometer is found useful (see, for example, Lowry and Parker, *Chem. Soc. Trans.* 1915, 1008). In the case of solids soluble in water it is necessary to use another liquid of known density which does not act on the solid. Petroleum, alcohol or carbon tetrachloride may be used, care being taken to determine the density of the particular liquid used. For a description of the precautions necessary in this method, see Tutton, *Chem. Soc. Trans.* 1894, 65, 650; 1897, 71, 865; Earl of Berkeley, *ibid.* 1907, 91, 56.

A method of finding the density of efflorescent or of very soluble solids has been described by Andreae (*Zeitsch. physikal. Chem.* 1913, 82, 109).

When the body the density of which is to be determined can be suspended by a piece of fine platinum wire and is non-porous, the piece is first weighed and is then attached by means of the fine platinum wire to the hook at

the bottom of a small scale pan. A vessel of water is placed under the scale pan, and the solid immersed in it. When a solid is thus immersed in water it displaces its own volume of water, and there is at the same time an apparent loss of weight; this is due to the surrounding water producing a pressure on the solid which is exactly equal to the pressure on the volume of water which the solid has displaced, and which previously kept the water in the vessel in equilibrium. The apparent loss of weight is therefore the weight of the quantity of water displaced by the solid, that is to say of an equal volume of water, so that we obtain the necessary data for determining the relative density of the solid at the temperature of the water at the time of the observation, the mass of the solid divided by the loss of weight in water being the density.

If the body is less dense than water it is obvious that its density cannot be determined precisely in this manner, for the solid will float. To cause it to sink, it is attached to a piece of metal of known weight and density. On weighing the two bodies together in water part of the apparent loss of weight is due to the displacement of the water by the metal and part to the displacement by the light body. The loss caused by the sinker can be calculated from its known weight and density, and this deducted from the total apparent loss of weight gives the weight of the water displaced by the body the density of which is to be determined.

In practice it is, however, better to determine the amount of water displaced by the sinker than to calculate it. The substance may first be weighed, and then the sinker attached by thin platinum wire to the scale-pan and weighed; then a vessel of water is placed under the scale-pan, and the sinker immersed in it. The apparent loss will give the quantity of water displaced by the sinker. The substance is now also attached to the wire and weighed, together with the sinker, in water, and the difference between the weight and the sum of the weights of the wire, sinker, and substance is the weight of the water displaced by the sinker and substance. As the weight of water displaced by the sinker has been determined, the difference between these two weights is the amount of water displaced by the substance alone, and the weight of the substance divided by this number gives the density.

The weight of water displaced by the light body may be obtained by the employment of three weighings, whereas the method just described requires four. It depends on the following facts: when a body floats on a liquid it displaces a weight of the liquid equal to its own weight; if the body is now totally immersed there is an upward pressure due to the additional quantity of the liquid displaced; this flotation pressure, determined by weights added to the weight of the body, gives the weight of the liquid displaced by the whole solid. In determining the density of such a body it is therefore necessary to know its weight, the apparent weight of the sinker when immersed, and the apparent loss of weight when the light body is attached to the sinker and weighed under water. The difference between the two last weighings, added to the weight of the body in

air, gives the quantity of water displaced by the solid. Thus if P is the weight of the light body, P' the weight of the sinker in water, and P'' the weight of sinker and the light body in water, the density $D = \frac{P}{P' - P'' + P}$.

Nicholson's hydrometer (as previously mentioned) may be used for the determination of the densities of solids. Weights are placed in the upper scale-pan until the instrument sinks to the mark. The weights are removed, and the substance is placed on the pan, and weights added until the mark is again at the level of the liquid; the difference between the weights is the weight of the solid in air. The solid is then placed on the lower scale-pan if of a higher density than water, or underneath the inverted cup if of a lower density, and weights are placed on the upper scale-pan to restore equilibrium. From the numbers thus obtained the amount of water displaced by the solid can be calculated, and from this, together with the weight of the body in air, the density is determined.

The following method of determining the apparent specific gravity of coke is recommended by F. Häusser (Ber. Ges. Kohlentechn. 1, 23). The sample piece, of suitable size, is ground to a roughly circular shape and dried until the weight is constant. It is then dipped, repeatedly if necessary, in melted paraffin wax so as to be coated with an unbroken layer, and weighed again. It is then weighed under water (J. Soc. Chem. Ind. 1922, 41, 207, A).

There are some solids which must not be wetted by any liquid, in consequence of a possible change of composition, and in these cases the usual methods of determining densities are of course not available. Others which are porous retain air so persistently that errors may arise by the presence of quantities of air which cannot be removed. In such cases an instrument similar to Say's stereometer (Ann. Chim. Phys. 1797, 23, 1) may be employed. This apparatus is now known as the volumenometer. The air inclosed in a glass bulb and adjoining tubes is shut off at atmospheric pressure; the space at the disposal of the air is then increased or decreased by a known amount, and the new pressure is read off on a manometer connected with the apparatus. These operations are repeated when the air space contains a known weight of the solid under examination and from the data obtained the density of the solid is calculated. Many forms of apparatus based on this principle have been described (Miller, Phil. Mag. 1834, 5, 203; Kopp, Annalen, 1840, 35, 17; Regnault, Ann. Chim. Phys. 1845, 14, 207; Grassi, J. Pharm. Chim. 1847, 11, 184; Baumhauer, Arch. Néerl. 1868, 385; Rüdorff, Ann. Physik, 1879, 6, 288; Paalzow, *ibid.* 1881, 13, 332; Bremer, Rec. trav. chim. 1898, 17, 263, 405; Mameli and Sanna, Gazz. chim. ital. 1902, 32, ii. 211; Zehnder, Ann. Physik, 1903, 10, 40). A description of one of the more recent modifications (Bremer's) will make clear the manipulation of the volumenometer. The wide-mouthed flask F (Fig. 16), immersed in a small water-bath, is connected through the three-way stopcock R with the tubes ab and cd , which contain mercury. On ab there are two marks or movable rings at p and q , the volume v of the tube between these being accurately known.

With the stopcock R turned so as to connect both F and ab with the air, the tube cd is adjusted until the top of the mercury meniscus is at p . The stopcock R is then turned so as to leave F and ab in connection but shut off from the air. The tube cd is now lowered until the top of the mercury meniscus in ab is at q , and the difference h in level between the mercury in the two tubes is determined with a cathetometer. A similar operation is carried out when

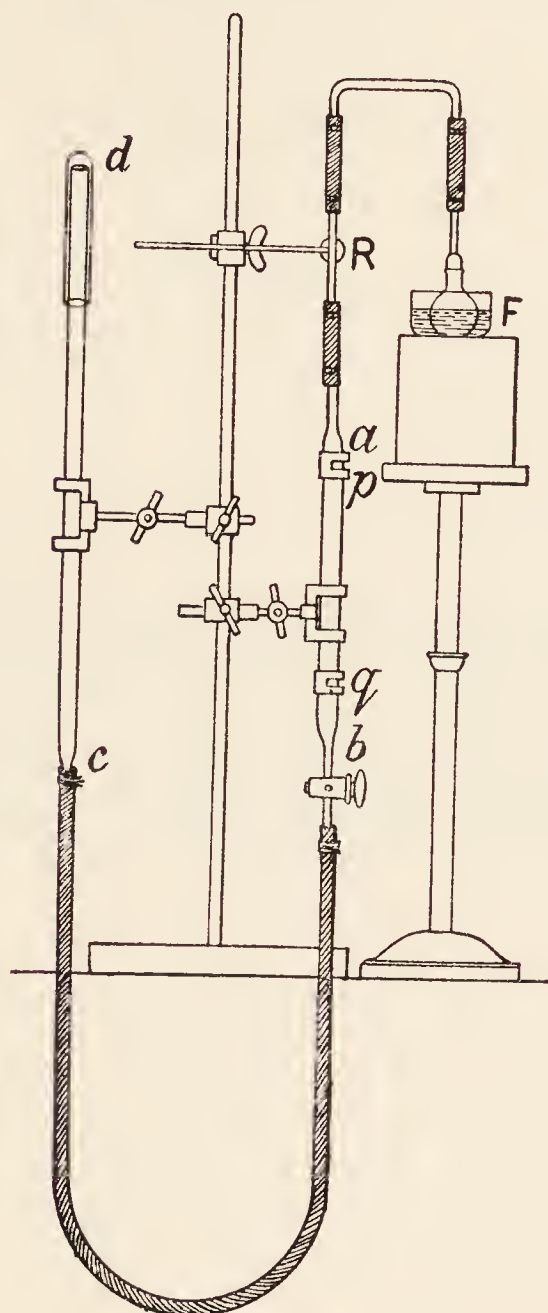


FIG. 16.

the flask F contains a weighed quantity of the solid under examination, the difference in level now found being h' . From these data the volume x of the solid can be calculated by the formula $x = vH \frac{h' - h}{hh'}$, where H is the barometric height.

The volumenometer obviously cannot be employed for the determination of the densities of solids which give off any gas or vapour under reduced pressure, such as efflorescent salts, for the increase of volume would be due not only to the expansion of the air in the apparatus, but also to the production of aqueous vapour. It answers very well for porous bodies like cotton wool, the entangled air from which at once expands on the pressure being diminished.

Occasionally it is necessary to determine the densities of small fragments of crystals or minerals, and for this purpose liquids in which the solids will just float may be used. The densities of the liquids may be afterwards determined, or a number of solutions of known

densities may be kept in readiness. It is obvious that the method is valid only when the solid is not acted on or dissolved by the liquid. For the application of this method, see Schaffgotsch, Pogg. Ann. 1862, 116, 279; Sonstadt, Chem. News, 1874, 29, 127; Church, Mineral. Mag. 1877, 1, 237; Goldschmidt, Jahrb. Mineral. Beilageband, 1881, 179; Klein, Compt. rend. 1881, 93, 318; Rohrbach, Ann. Physik, 1883, 20, 169; Brauns, Jahrb. Mineral. 1886, ii. 72; Retgers, Zeitsch. physikal. Chem. 1889, 3, 289; 4, 189; 1893, 11, 328; Jahrb. Mineral. 1896, i. 212; ii. 183. Among the heavy liquids used by these authors are a solution of the double iodide of potassium and mercury, which can be obtained of the density 3.196; a solution of cadmium borotungstate (density of saturated solution 3.281); a solution of mercuric and barium iodides, which can be obtained of the density 3.588, but is unstable on mixing with water; a saturated solution of lead perchlorate, sp.gr. 2.6 (Thiel and Stoll, Ber. 1920, 53, 2003), and methylene iodide (density 3.3). In the first cases, water is added if a liquid of lower density is required, while benzene is similarly used with methylene iodide. Liquids, the density of which is varied in the way described, are used not only for determining the density of minerals, but also for separating the constituents of mixed minerals. The following three liquids, useful for the mechanical separation of minerals of different densities, are colourless and may be diluted and recovered: aqueous barium bromomercurate solution, d^{11} 3.11, d^{18} 3.14; saturated aqueous thallium formate solution, d^{10} 3.31, d^{20} 3.40, d^{50} 4.10; aqueous solution of thallium formate and thallium malonate in equal proportions, d^{10} 4.00, d^{50} 4.70, $d_{\text{about } 100}$ above 5. Thallium formate, melting at 95° to a highly mobile liquid, may also be used, and a mixture of thallium formate and malonate in equal amounts melts below 95° , and has d above 5. Fused thallium formate has d below 5, but it dissolves powdered thallium carbonate, giving a liquid with d above 5 (Clerici, Atti R. Accad. Lincei, 1922, [v.] 31, i. 116). Other fused solids have been employed for a similar purpose (see, for example, Thoulet, Compt. rend. 1878, 86, 454; Klein, *l.c.*; Bréon, Compt. rend. 1880, 90, 626).

The floating method of determining the specific gravity of solids has been utilised also in the examination of fats (Hager, Zeitsch. anal. Chem. 1880, 19, 239). In this case the liquid medium is a suitable mixture of water and ethyl alcohol.

For an application of the flotation method in determining the density of graphite, see Ryschkewitsch and Köstermann (Zeitsch. Elektrochem. 1924, 30, 86).

It has been suggested (Andreae, Zeitsch. physikal. Chem. 1911, 76, 491) that the foregoing method may be advantageously varied by putting the crystals under examination along with a mixture of methylene iodide and benzene of about the same specific gravity in a dilatometer. This is placed in a bath the temperature of which is slowly altered until the crystals float. From the weight and volume of the dilatometer the density of the liquid can be accurately determined.

J. C. P.

SPECTROSCOPY. I. Introduction. When

Fraunhofer investigated the solar spectrum he designated the most strongly-marked lines in the visible region by the letters of the alphabet, starting from A at the red end with a wave-length of 7600 ten-millionths of a mm. to K at the violet end with a wave-length of 3930 ten-millionths of a mm. When the extension of the solar spectrum into the ultra-violet region was discovered by photographic methods this lettering of the principal lines was continued into this region as far as the wave-length 2950 ten-millionths of a mm., the letters L to U being used. Owing to the absorption exerted by the great thickness of air through which the light has to pass, the solar spectrum does not extend much beyond the limit of about the wave-length 3000 ten-millionths of a mm.

Recent investigation has shown that oxygen has an absorption band for light of very short wave-length, and that even with an extremely thin layer of oxygen at atmospheric pressure this absorption extends up to at least as far as 1800 ten-millionths of a mm.

It is evident that this absorption sets a lower limit beyond which it is impossible to investigate the ultra-violet spectrum unless a vacuum spectrograph is employed.

Owing to their great convenience as landmarks in the spectrum the Fraunhofer lettering of the principal lines is still used very largely, and in Fig. 1 is shown a diagram in which these principal lines are set out according to their wave-lengths. The elements to which these lines are due are marked at the bottom of the diagram. It may be remarked that A and B are, in reality, absorption lines due to the atmosphere. As regards the extension of the spectrum into the invisible region beyond the red, usually called the infra-red, a considerable portion has been investigated by photographic methods using specially prepared plates. The radiation in this part of the spectrum partakes of the nature of heat, and therefore may readily be investigated by instruments sensitive to heat rays, such as thermopiles, radiometers, radiomicrometers, or bolometers. With these instruments investigations have been pushed to an extraordinary distance, and in one case radiations have been detected in the emission spectrum of a quartz mercury vapour lamp with a wave-length of 3,160,000 ten-millionths of a mm. The measurement of absorption bands has been extended for a considerable distance beyond this limit, both by direct and indirect methods. By indirect methods it has been found that substances exhibit characteristic absorption bands at wave-lengths nearly ten times as great as the above.

Owing to the fact that recently a new spectroscopic standard was set up based upon measurements of the wave-length with interference apparatus, it will perhaps be advisable to define the various units now used in spectroscopy. The original unit of wave-length used by Ångström himself in his measurements was the ten-millionth of a mm., which is often called the tenth-metre since the unit is 10^{-10} metre. About the year 1890 a new standard of wave-lengths was introduced by Rowland who, basing his measurements upon the well-known coincidence method with gratings, determined the wave-lengths of a very great number of the Fraunhofer lines.

From that time until quite recently all spectroscopic measurements were referred to these solar standards of Rowland.

Not long after Rowland published his map, Michelson, by means of interference methods, determined the wave-length of the red cadmium line with exceedingly great accuracy with reference to the standard metre in Paris. Fabry and Perot then, by somewhat similar inter-

ference methods, determined the wave-length of a number of iron lines and solar lines in terms of Michelson's value, and showed that there is a periodic error in Rowland's scale.

As the result of Fabry and Perot's work the International Union for Solar Research decided to adopt as secondary standards of all spectroscopic measurements the means of the values obtained by three independent observers of the

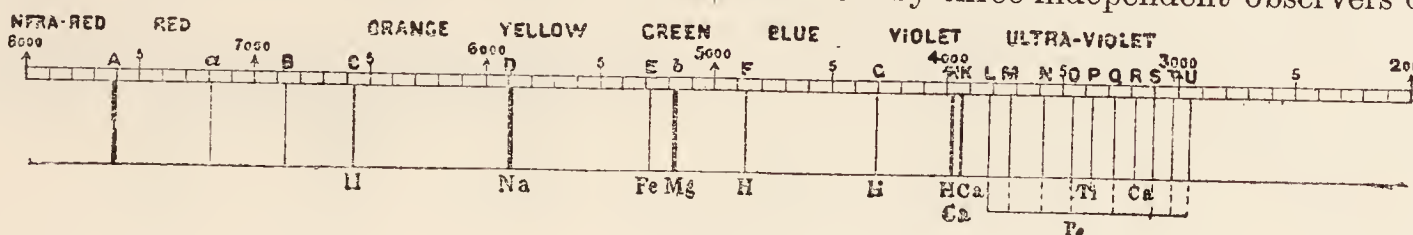


FIG. 1.

wave-lengths of various lines in the spectrum of the iron arc. As all these observations are determined in relation to Michelson's value of the red cadmium line, the International Union decided that the primary standard for spectroscopic measurements shall be the wave-length of the red line of cadmium $\lambda = 6438.4696$ Ångströms, and that the Ångström shall be so defined. This unit only differs from the original Ångström unit by less than one part in 10 million. It has also been agreed that all wave-lengths expressed in terms of this standard shall be denoted by the symbol I.A. Since the difference between the new unit and the old Ångström unit is so small it may still be spoken of as the tenth metre, and therefore it may be said that the wave-length of the red cadmium line is $\lambda = 6438.4696$ Ångströms or 10^{-10} metres, or 643.84696μ or 0.64384696μ . The units μ and $\mu\mu$ are more especially used in cases of the long wave-lengths which, of course, cannot at present be measured with such great accuracy.

It has been further agreed that tertiary standards shall be determined by interpolation between the secondary standards. A number of these secondary and tertiary standards in the arc spectrum of iron and in the neon spectrum were adopted in 1922, the neon lines being suitable for use in the orange and red regions. These wave-lengths may therefore be used in all cases where great accuracy is required.

II. The spectroscope. The limits of absorption exerted by various materials are given below, and from these it may be seen that in spectroscopes, designed for the examination of the visible spectrum, the optical parts may be made of glass, whilst for the examination of the ultra-violet and infra-red rays some other material transparent to one or other of these regions must be substituted.

(a) *Direct-vision spectroscope.*—The simplest form of visual spectroscope is the direct-vision instrument in which the dispersion of a very wide-angled dense flint-glass prism is partially corrected by crown-glass prisms. Since in this way it is possible entirely to correct the deviation of the mean rays of the spectrum and only partially correct that of the extreme rays, a spectrum will be produced.

The usual arrangement of such an instrument is shown in Fig. 2, where the centre prism p' is made of dense flint glass, and the two outer

prisms p, p , of crown glass. In Fig. 3 is shown the complete instrument, which is provided with a slit and eye-piece. This direct-vision spectroscope is very useful for the qualitative investigation of flame spectra or absorption spectra in the visible region, but although in some cases arrangements are made whereby readings of the position of lines or absorption bands can be

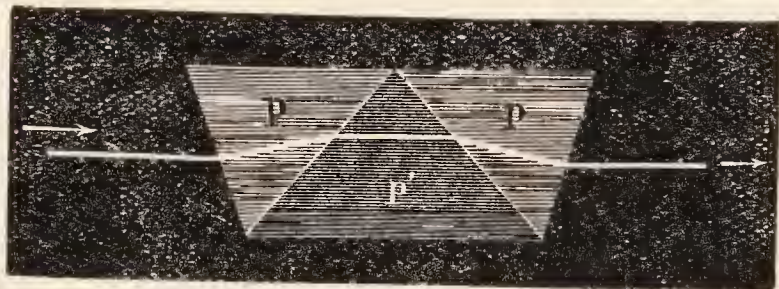


FIG. 2.

made upon some form of scale, yet it is clear that such measurements can only be very rough.

(b) *Spectrometer.*—For more accurate visual work some form of spectrometer must be used, the term spectrometer being applied to a spectroscope in which some device is at hand for the more accurate reading of the deviation of the lines or their actual wave-lengths. In the first case by means of a graduated arc the angular deviation of the lines may be read off, and from

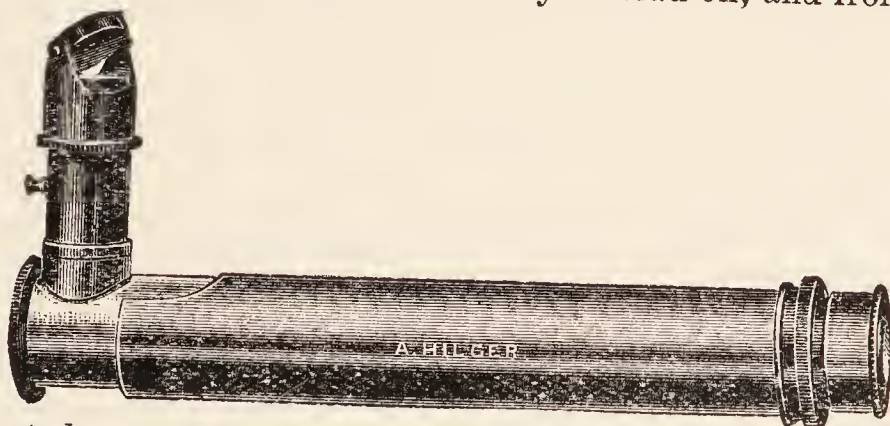


FIG. 3.

these the wave-lengths of the various lines may be obtained, either by the method of graphical interpolation, or by means of a simple interpolation formula as described below. It has been found possible, however, by the use of a constant deviation prism to construct a simple form of spectrometer by means of which the wave-lengths of the lines in the visual region can be read off directly. This instrument is shown in Fig. 4, and is of the fixed arm type, that is the collimator and telescope are rigidly fixed and the spectrum is made to pass across the

field of view of the telescope by rotating the prism. The rotation of the prism is carried out by means of a micrometer screw carrying a drum head, which is so divided that the wave-length of any line under observation may be directly read off. In the best form of the instrument the accuracy of the reading is about 1 Ångström.

(c) *The spectrograph*.—In accurate work upon the measurement of the wave-lengths of spectrum lines it is necessary to have recourse to photographic methods for two reasons, firstly, a permanent record of the spectrum is thereby obtained which may be measured at leisure; and in the second place, the photographic plate is sensitive to the ultra-violet region, which indeed is of far greater importance than the visible region, since the former generally contains the most characteristic lines of the elements. It is, of course, possible to fit a photographic attachment to either of the spectroscopes mentioned above, yet it is far preferable that the optical parts of the instruments be made of quartz.

The construction of a spectrograph with glass optical parts is simplified by the fact that it is possible to use achromatic lenses which give a flat field upon a photographic plate. It has also been found possible to make achromatic

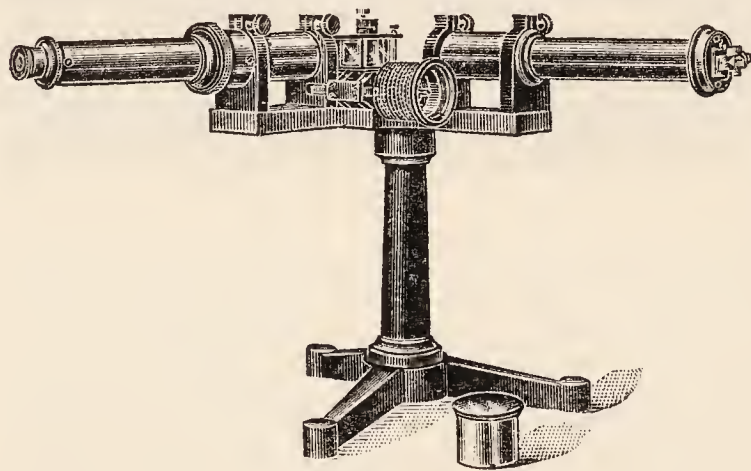


FIG. 4.

lenses with quartz-calcite or quartz-fluorite combinations. To the first of these there is the objection that calcite exerts an absorption beginning at $\lambda=2200\text{\AA}$, and to the second there is the objection arising from the scarcity of fluorite. It will generally be found, therefore, with a spectrograph the lenses and prisms of which are made of quartz, that the foci of the various spectrum lines lie upon a curve, so that photographic films must be used. Recently, however, there have been introduced spectrographs with quartz prisms and lenses so cut in relation to the optic axes that the whole spectrum from $\lambda=8000\text{\AA}$ to $\lambda=2100\text{\AA}$ may be photographed on a flat plate in good focus.

An essential point is that the photographic plate must be set at an acute angle (27°) with the axis of the telescope lens. An illustration of one of these instruments is shown in Fig. 5.

It is convenient in any spectrograph to have a wooden screen placed in front of the photographic plate, and in this screen to cut a narrow horizontal slot to allow the passage of the spectrum to the photographic plate. The dark slide carrying the plate may then be so mounted as to be capable of movement up and down by means of a rack-work adjustment so that several photographs may be taken upon the same plate.

Since the determination of wave-lengths in general practice is always carried out by interpolation between lines of known wave-length photographed upon the same plate, it is necessary that the two spectra, the unknown one and the standard, be photographed in juxtaposition. This is most conveniently carried out by the use of draw-slides fitted over the slit, so that any

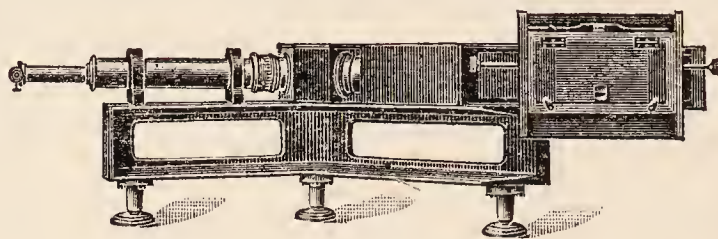


FIG. 5.

portion of the slit may be exposed at will. The two spectra to be compared are successively photographed through two adjacent portions of the slit, when, of course, it will be found that they are in juxtaposition on the photograph.

It must not be forgotten that, unless precautions are taken, errors may readily be introduced owing to the spherical aberration of the spectrograph lenses. Unless the same portions of the lenses are used in comparing two spectra, it will generally be found that these are not in correct relation to one another upon the photographic plate. If a condensing lens is used to focus an image of the source of light upon the slit, then it is easy enough to obtain photographs of the two spectra in correct relation to one another. The condensing lens is fixed in such a position that its axis passes through the centre of the slit and the centre of the collimating lens, and also at such a distance from the slit that an image of the source may be focussed upon the slit. When the spectra of two sources have to be accurately compared, one of these is placed in such a position that its image is thrown upon a portion of the slit of the spectrograph. A photograph is then taken of the spectrum and, without closing the dark slide carrying the plate, the first source is removed and the second so placed that its image is focussed upon the slit a little above or below the position previously occupied by the first source, and then the second photograph is taken. In carrying out this procedure it will be seen that the draw-slides mentioned above will prove of excellent service.

A very convenient form of spectroscope is one in which a grating is substituted for prisms. A grating may be obtained which has been accurately ruled on a polished surface of glass or speculum metal. The former are used as transmission instruments, whilst in the latter case the spectrum is obtained by reflection.

In a prism spectroscope the dispersion increases with decrease of wave-length, and so the blue and ultra-violet regions appear more extended than the red and orange. In the case of a grating which produces the spectrum by diffraction, as the diffraction is a function of the wave-length, it will be found that the distribution of rays in the spectrum will be much more nearly proportional to their wave-length. Thus, for example, in the visible spectrum it will be found that the yellow rays occupy the middle position. For this reason the dispersion given by a grating is relatively

greater in the red and yellow than that given by a prism spectroscope, and hence there is some advantage in using a grating for the study to these regions.

Owing to the difficulty of successfully ruling a grating the cost is necessarily rather high, but it has been found possible to produce excellent replicas at a very reasonable cost. These replicas are produced by making a celluloid cast of a first-class ruled grating. The casts are then mounted upon a flat glass plate, and may be used exactly in the same way as a ruled grating. With spectrographs of the above type it is possible to obtain photographs of spectra to as far as the wave-length of 2200 Å, this limit being set by the absorptive power of the gelatine on the photographic plate.

For the investigation of the ultra-violet region beyond this limit it becomes necessary to eliminate this and also to employ a vacuum spectrograph so as to avoid the absorption exerted by air and other gases. A considerable amount of work has already been carried out on the emission spectra of elements in this most important region, and there has recently been introduced a vacuum spectrograph designed for investigation of this very short wave-length region of the spectrum. This instrument is fitted with a reflecting grating ruled on a concave mirror so that all lenses are avoided, and it is readily possible with its aid to obtain photographs of emission spectra to as far as 500 Å. This region is often spoken of as the Schumann region, after the first physicist to explore it. Schumann succeeded in preparing photographic plates on which a layer of AgBr had been deposited containing only a minute quantity of gelatine. By a slight modification of his process photographic plates may be prepared for this special work which retain their sensitivity for some months, and indeed, such plates are now on the market.

III. Photography of the spectrum. A few words may be said about the photographic plates to be used in spectrum work. For the blue and ultra-violet regions any good make of plate may be employed, but it is to be remembered that in general better definition is obtained with slow than with rapid plates. If very faint spectra have to be photographed, Wood advises the exposure of the plate for a few moments to a very weak light, such as that obtained from a small gas flame. The actual time for this exposure must be found by trial for the make of plate used, and in one case Wood found that 4 seconds' exposure of the plate to the light from a gas flame turned down until the yellow tip is only 3 or 4 mm. high at a distance of 2 metres was necessary. This exposure may be made either before or after the spectrum photograph is taken.

For the yellow and red regions panchromatic plates may be used. A good panchromatic plate, such as the Ilford make, gives excellent results, its sensitiveness extending to about 8000 Å. In using this type of plate it is advisable that the development be carried out in total darkness.

If it be required to photograph the regions of greater wave-length than $\lambda=8000$ Å, special methods have to be employed for the production of plates sensitive to this region.

Three different methods have been used for

this purpose. First Abney prepared special emulsions at a low temperature with which he coated the glass plates. This method has been made more practicable by Ritz. The second method depends on the inverse action of the infra-red rays upon an ordinary photographic plate, which previously has been solarised by exposure for a short time to a weak light. This method has been used by Millochau, who succeeded in obtaining photographic records up to $\lambda=10000$ Å. The third method is that known as the phosphorographic method, and depends upon the power possessed by infra-red rays of destroying the phosphorescence of zinc sulphide. Bergmann, in using this method, exposed a zinc sulphide screen for 1-2 mins. to an arc light, a second screen of a saturated solution of cupric ammonium sulphate being interposed. The screen is then exposed to the spectrum for 2-8 mins., and then brought into contact with the photographic plate, which after 2 hours is developed. In this way it has been found possible to reach as far as 20,000 Å.

IV. Recognition of lines and determination of wave-lengths. In any work upon qualitative analysis by spectroscopic methods, or in the quantitative estimations described below, it is essential to recognise the lines in any known spectrum, which may most easily be carried out by a determination of their wave-lengths. This is simple enough for the lines in the visible spectrum when a direct-reading wave-length spectrometer is used.

In the older form of spectrometer, in which the deviations of the lines are read, or their position on some arbitrary scale noted, it is necessary to reduce the values obtained to wave-lengths. This may be done either by the method of graphical interpolation or by the use of Hartmann's interpolation formula. In the former case the deviations of certain well-known spectrum lines, or their scale readings, are plotted against the wave-lengths on squared paper. When a sufficient number of such points are obtained a curve is drawn through them; the wave-length of an unknown line may at once be read from this curve if its deviation or scale-reading is known. For drawing the dispersion curve in the visible region Collie has pointed out that a vacuum tube containing helium, hydrogen, and mercury vapour gives a number of lines eminently suited for the purpose. The wave-lengths and wave-numbers of the lines in this spectrum are as follows:—

		Wave-lengths	Wave-numbers
Helium	. . red	7065	14197
Helium	. . red	6678	14969
Hydrogen	. . red	6563	15232
Mercury	. . orange	6152	16250
Helium	. . yellow	5876	17014
Mercury	. . yellow	5791	17265
Mercury	. . yellow	5770	17329
Mercury	. . green	5461	18307
Helium	. . green	5016	19932
Helium	. . green	4922	20311
Hydrogen	. . blue	4861	20564
Helium	. . blue	4713	21211
Helium	. . violet	4471	22357
Mercury	. . violet	4358	22937
Hydrogen	. . violet	4340	23031

It will also be found that a vacuum tube containing neon shows a spectrum containing a great number of lines in the red, which are exceedingly convenient for the calibration of the red region.

It will be noticed that if instead of the wave-lengths the wave-numbers of the lines be used, the shape of the curve becomes flatter and easier to draw. By the wave-number is meant the number of wave-lengths contained in 1 cm. *in vacuo*, i.e. the reciprocal of the wave-length reduced to a vacuum. In order to reduce the wave-length of any line measured in air to its real value *in vacuo*, it is necessary to multiply it by the refractive index of air for the particular wave-length. In making this correction in actual practice it is simplest to add a small number to the wave-lengths. A table of these corrections can be readily constructed, and they lie between 2.5 Ångström at $\lambda=8000$, and 0.7 Ångström at $\lambda=2000$. Such a table is given complete in Twyman's Wave Length Tables.

If it be desired to draw the calibration curve from photographic measurements it is simply necessary to measure the distances between the lines on the plate, starting from a chosen line at either end of the spectrum, and plot these against the wave-numbers or wave-lengths.

As in this case the photographic record will no doubt include the ultra-violet region, the above list of wave-lengths will not, of course, be sufficient. A very convenient set of lines for this purpose is given in the spark spectrum of gold, and the following table contains the wave-lengths and wave-numbers of the principal lines of gold and silver, such as are given by gold of ordinary purity. As there are not many strong lines of gold in the red, orange, and green, one or two lines of lithium, sodium, and nitrogen have been included.

No.	Wave-lengths	Wave-numbers	Element and intensity	No.	Wave-lengths	Wave-numbers	Element and intensity
1.	6708.2	16379	Li 10	23.	2641.6	37843	Au 6
2.	6457.0	15483	Au 5	24.	2590.2	38595	Au 6
3.	6378.4	15927	Au 4	25.	2544.3	39292	Au 5
	5896.2	16955	Na 10	26.	2503.4	39934	Au 8
	5890.2	16973	Na 10	27.	2473.9	40409	Ag 8
4.	5837.7	17127	Au 6	28.	2447.9	40839	Ag 8
5.	5679.8	17601	N 12	29.	2437.8	41008	Ag 10
6.	5465.5	18291	Ag 10	30.	2428.1	41172	Au 10
7.	5230.5	19114	Au 8	31.	2413.2	41427	Ag 10
8.	5005.7	19978	N 10	32.	2387.9	41865	Au 4
	5002.7	19983	N 10	33.	2364.8	42274	Au 10
9.	4792.8	20863	Au 8	34.	2352.8	42490	Au 6
10.	4488.4	22273	Au 8	35.	2331.3	42881	Ag 8
11.	4315.4	23167	Au 8	36.	2304.9	43377	Au 8
12.	4065.2	24592	Au 15	37.	2283.4	43781	Au 5
13.	3898.0	25647	Au 10	38.	2242.7	44576	Au 5
14.	3586.7	37873	Au 7	39.	2229.1	44848	Au 6
15.	3383.0	29551	Ag 10	40.	2201.4	45408	Au 5
16.	3280.7	30472	Ag 10	41.	2189.0	45663	Au 5
17.	3122.9	32013	Au 10	42.	2166.6	46141	Ag 4
18.	3029.3	33001	Au 6	43.	2145.7	46590	Ag 3
19.	2913.6	34311	Au 9	44.	2125.3	47038	Au 5
20.	2825.6	35381	Au 6	45.	2110.8	47361	Au 6
21.	2748.3	36375	Au 5	46.	2082.1	48013	Au 5
22.	2676.1	37358	Au 12				

For the recognition of the lines in the spectrum and for a measurement of their wave-length Hartmann's interpolation formula will prove of great service. In its original form this formula is as follows:—

$$\lambda = \lambda_0 + \frac{c}{(n_0 - n)^{\frac{1}{a}}}$$

where λ_0 , c , n_0 , and a are constants, and n is the linear distance of the line measured from some line chosen as origin. Hartmann showed, however, that since a is nearly = 1 it may be omitted, which simplifies the formula considerably. As may readily be seen, the values of λ_0 , c , and n_0 may be obtained if the wave-lengths and scale readings of three lines in the spectrum be known. It is advisable, of course, that one of these lines be chosen near the middle of the region of the spectrum which is being dealt with, and that of the other two lines, one be chosen at the beginning and the other at the end of the region measured. When the values of the three constants have been found, the wave-lengths of any line can at once be calculated from its scale reading. Although the formula gives more accurate results when short lengths of the spectrum are being dealt with, yet it may be applied over a considerable range with very fair accuracy, and if it only be required to recognise the various lines in a spectrum, the accuracy then given is quite sufficient.

If, however, it is required to measure the wave-length of any new spectrum lines, or if for any other reason greater accuracy is required than can be obtained from Hartmann's formula, the measurement of the wave-length of any line may be found by a simple interpolation between two known lines in the comparison spectrum. Since in a prismatic spectrum the dispersion steadily increases as the shorter wave-lengths are approached, it is advisable in the interpolation to choose two standard lines of known wave-length which are near together, and, of course, one on each side of the line, the wave-length of which is to be measured.

A simple method of approximately determining the wave-lengths of lines from photographs of prismatic spectra has been devised by Edser and Butler. This method consists in photographing a series of interference fringes adjacent to the spectrum to be measured; these interference fringes are produced by Fabry and Perot's method, which consists in causing a beam of white light to pass through a film of air bounded by two parallel sides of half-silvered glass. When this light is examined in a spectroscope, a continuous spectrum is seen, crossed by a series of interference fringes. A sufficiently accurate interference apparatus can be made by taking two pieces of good plate-glass about 3 ins. square, which are each half-silvered on one face; the plates are then carefully dried and mounted together, the two silvered faces turned towards one another. The plates are fastened together by a little wax placed all round the edges, when perfect adjustment can be obtained by simply pressing the plates together with the fingers. A preliminary adjustment for parallelism is made as follows: a spot of light or an incandescent electric lamp is viewed through the silvered surfaces; a long train of images

due to multiple reflections is generally visible. These images are brought into coincidence, and then, on examining a sodium flame through the apparatus, interference bands will generally be visible. The final adjustment for parallelism is made with the help of these bands, which should be made as broad as possible. In carrying out this adjustment the film is held as close as possible to the eye, because for a parallel air film viewed normally the interference bands are formed at an infinite distance. The perfection of the results finally obtained will depend greatly on the accuracy of this adjustment.

The slit of the spectroscope is illuminated by a slightly convergent beam of light from an arc lamp, and the plates are placed in front of the slit, and as near to it as possible; under these circumstances the spectrum will be found to consist of a series of bright lines separated by black intervals. The best results will be obtained when the plates are in such a position that the slit is parallel to the direction of the interference bands seen with sodium light. The closeness of the bands depends upon the thickness of the film between the silvered surfaces. By means of draw slides, or screens upon the slit, these interference bands are photographed adjacent to the spectrum which is to be measured.

If the interference fringes on a photograph be numbered consecutively, starting from either end, the wave-numbers of all the fringes will be in linear proportion to their order number.

The wave-numbers of one or two lines at each end of the photograph are plotted against their readings on the interference fringe scale, and a straight line is drawn through the points thus obtained. From this straight line the wave-number of any spectral line can be found at once from its scale reading.

V. Methods of illumination. Except in the case of phosphorescent spectra all substances are caused to luminesce when in the state of gas. The following methods of illumination are most usually employed: Flame, electric arc, electric spark, and high potential discharge through gases under reduced pressure.

(a) *Flame spectra.*—Usually in the case of flame spectra the most convenient flame is that given by the Mecker burner. If it be possible to use an aqueous solution of the salt to be examined, a lasting effect is obtained by the use of the apparatus first designed by Mitscherlich, and which is shown in Fig. 6. The wick at the bottom is composed of fine platinum wires or quartz fibres. A little ammonium acetate added to the solution of the salt is useful in order to make it run well along the wick. In the case of solid substances Hartley recommends as support for the substance thin strips of cyanite or a mixture of carborundum and porcelain clay, which has been fired at a high temperature. It is also

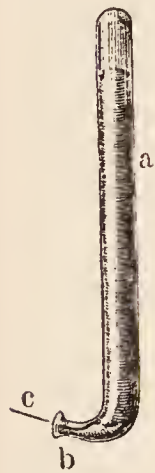


FIG. 6.

convenient in some cases to use a small spoon made of fused silica. Hartley also recommends feeding the burner with gas containing a little chloroform vapour in order to obtain a lasting chloride spectrum.

Again, a very convenient method of obtaining flame spectra is to introduce into the flame very

finely-divided particles of the element itself or of the solution of a salt. In the case of the former, as has been shown by Hemsalech and de Wattleville, the air supplied to the burner is passed through a small bulb in which is maintained either a series of electric sparks, or the electric arc between poles of the element to be investigated. In the latter case, the coal-gas supplied to the burner is passed through a flask containing a solution of the salt. This solution is made strongly acid with hydrochloric acid, and a few fragments of zinc are added. The bubbles of hydrogen thereby evolved carry with them into the burner a very fine spray of the solution. An alternative method is to use some form of 'vaporiser' or 'atomiser' by means of which the solution is broken up into very fine spray which is caused to mix with the illuminating gas before it enters the burner.

(b) *Arc spectra.*—In the case of the electric arc, when the spectra are required of metals which are not easily fusible, the arc may be made between poles of the metal itself or the positive pole (which is the hotter) may be made of carbon. An alternative method is to use a carbon arc and put the substance to be examined in small portions into the crater formed in the positive pole. This, however, has the inconvenience of causing the arc to jump rather badly. A much steadier effect is obtained by using as the positive pole a cored carbon rod in the central hole of which has been packed the substance, the spectrum of which is to be examined. When carbon poles are used for the production of the arc spectra of substances it will, of course, be found that the spectrum shows the lines and bands due to carbon. These may be eliminated by comparing the photographs with one taken of the arc between two pure carbon poles.

(c) *Spark spectra.*—The third method of illumination is to pass electric sparks from an induction coil or transformer either between electrodes of a metal or between beads of metallic salts which have been melted on to the ends of platinum wires or between an electrode of gold, platinum, or graphite, and the solution of a salt.

In the first case, it is advisable to use a condensed discharge, which may be produced by the introduction of a Leyden jar or plate condenser connected in parallel with the sparking apparatus. It may be pointed out that the most suitable capacity of condenser depends very largely on the size of the induction coil or transformer, and no very definite directions can be given. The condenser should be so chosen that the size of the spark obtained between iron electrodes in air is of the order of 2–3 mm. For the study of the spark spectra of melted salts de Gramont uses two platinum wires, one of which is mounted in a horizontal position, and the other is set above the first, making a somewhat narrow angle with it, so that the two extremities are close together. The two ends of the wires are heated in the Bunsen burner, and a small fragment of the required salt is melted on to the end of the upper wire. The sparks are then passed between the lower wire and the melted bead.

For the study of spectra of solutions a convenient form of apparatus is shown in Fig. 7.

In this apparatus the lower platinum wire is surrounded by a narrow, thin glass tube up which the solution ascends by capillary attraction. Another form of sparking apparatus due to Hartley is shown in Fig. 8. In this the electrodes are made of graphite, which is cut into the shape of wedges about $\frac{1}{4}$ in. long and $\frac{1}{8}$ th in. wide. The wedges are set with their edges parallel to one another, and to the collimating tube of the spectroscope. The wedges are attached to platinum wires and are fixed in glass tubes. The lower wedge dips into the solution, which ascends by capillary attraction up the deep grooves or scratches.

A third apparatus, especially designed for the investigation of quantitative spectra, was used by Hartley and by Pollok, and may be thus described. A piece of glass tube about 6 ins. long and with a capillary bore is bent into the form of a U-tube with the limbs of unequal length and a small cup, like a thistle funnel, of about 2 c.c. capacity is blown at each end as shown in Fig. 9. A gold

wire is then passed through the capillary of the tube so as to project a little above the rim of the lower cup, and a small piece of thin-walled capillary tubing is slipped over the end of the gold wire, and is just so long as to reach the top of the wire and thus draw up the solution and keep the top of the wire well wetted when sparking. It is

the metallic electrodes from the spectrum of the salt.

The phenomena which may be seen in a spark discharge are somewhat complex, for the condensed spark consists of different zones, there being a central part which is very brilliant and is surrounded by an aureole. A spectroscopic examination of the spark shows the rays emitted by the whole spark, aureole, and central portion, and also the rays which are emitted only by the central portion. These two different sets of rays can be recognised as long and short lines in the photograph of the spectrum.

Generally when dealing with spark spectra it is advisable to use a condenser, but in some cases, as will be referred to below, advantageous results are obtained by using the uncondensed spark discharge. It must not be forgotten that in any spark spectra will be found many of the spectrum lines of air. These latter are more pronounced, the less volatile is the substance under examination; for example, the air lines will be found to be very strong in the spectrum of the spark between platinum electrodes. These air lines may readily be eliminated from a spectrum by comparing it with the spectrum of the spark, say between platinum electrodes, when, of course, the lines common to the two spectra will be those due to air. It was shown by Hemsalech that the air lines may be entirely eliminated from any spectrum by introducing self-induction into the secondary circuit. A self-induction coil may be made quite readily by winding wire round a bobbin, the coil so prepared being put in series with the sparking apparatus. The amount of self-induction to be introduced of course varies with the size of the induction coil used. Such a self-induction coil for use with a large Ruhmkorff induction coil is 50 c.c. long, 5 cms. internal diameter, and contains 8 layers of wire each consisting of 150 turns.

(d) *Spectra of gases*.—The most convenient method for the illumination of gases is to pass the discharge from the induction coil through them under a pressure of from 1 to 3 mm. The gas is enclosed in a vacuum 'tube,' which has two electrodes and a capillary portion, as first designed by Plücker. It will be found that the discharge through the capillary portion of the tube is exceedingly brilliant. If the ultra-violet region of the spectrum is required, either the whole vacuum tube may be made of quartz with no electrodes, or the discharge through the capillary may be viewed end-on through a quartz window.

For the methods employed for making and filling these tubes reference must be made to books on gas manipulation.

(e) *Phosphorescent spectra*.—An important method of illumination, especially in the study of the rare earths, is that of the cathode streams producing phosphorescence in the substance under examination. It has been found as a result of researches by Crookes, Lecoq de Boisbaudran, Urbain, and others, that very many minerals and artificially-prepared substances give characteristic phosphorescent spectra, but this method of examination finds its chief practical use in connection with the separation of the rare earths from one another.

The rare earth under investigation in the



FIG. 7. wire is then passed through the capillary of the tube so as to project

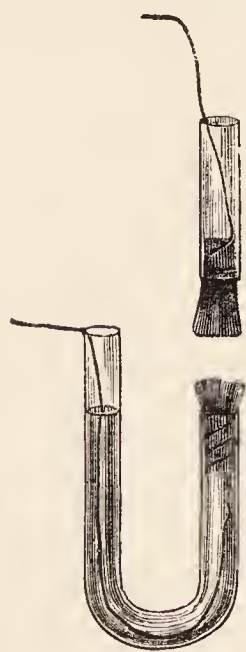


FIG. 8.

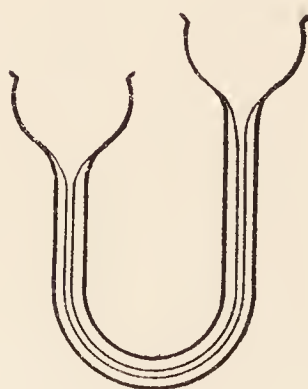


FIG. 9.

necessary to employ fairly thick gold wire, and it may be found economical only to use a short piece of gold attached to a thin platinum wire sufficiently long to pass through the capillary. The electrode in the solution must be made the negative, and the upper or positive electrode may be held in any convenient manner, and the spark should not be too long.

Two very convenient pieces of apparatus for obtaining the spark spectra of solutions without the use of metallic electrodes are described by Krulla, the principle being that the spark is made to pass between two jets of the solution. This method eliminates the spectrum lines of

form of oxide or sulphate is placed in a bulb tube provided with two electrodes consisting of flat plates of aluminium, the normals to which lie in the direction of the centre of the heap of material to be examined. Since the cathode rays leave the electrode normal to its surface, it is evident that this construction will give the maximum brilliancy. The exhaustion of the tube is carried to a very high point, the exact degree of exhaustion being judged by the maximum of phosphorescence obtained. For the examination of the spectrum the tube is set at a slight angle, so that the phosphorescent rays can be directed into the spectrograph. When the ultra-violet region is to be examined the phosphorescence tube is provided with a quartz window cemented on and through which the phosphorescent spectrum may be photographed.

VI. Absorption spectra. By an absorption spectrum is meant a continuous spectrum from which certain definite rays, or groups of rays, have been removed during the passage of the light through the substance under examination. The rays which are found to be wanting in the transmitted beam of light have been absorbed by the material investigated, this being due to the fact that the molecules of the substance possess the power of selectively absorbing energy of definite frequencies. During recent years the study of the absorption spectra of elements and compounds has developed into a very important branch of spectroscopy, both on account of the attempts that have been made to correlate the absorption spectrum of a compound with its constitution and also because it has more recently been found that the whole problem of chemical reaction and reactivity is directly connected with the radiant energy absorbed by substances.

The technique of absorption spectra measurements differs somewhat from that employed in emission spectra work and may be very briefly described. It is necessary to determine not only the wave-lengths or frequencies of the radiant energy that is absorbed, but also the amount of the energy that is absorbed by a given thickness of the substance under investigation. Obviously, therefore, in addition to the measurement of the wave-lengths, the relative intensities of the radiant energy from the source before and after transmission through the absorbing layer must be determined. In the investigation of the absorptive power of substances in the infra-red region a very convenient source of the radiant energy is a platinum wire uniformly coated with clay which is heated by a constant electric current.

The energy falls on the slit of a suitable spectrometer with rock salt prism and concave mirrors or with a grating, and the intensity at a given wave-length is determined by a thermopile and galvanometer or by a radiometer. A known thickness of the substance under investigation is then placed outside the slit and the intensity of the transmitted beam measured. From these two measurements the percentage amount of the energy at the selected wave-length is obtained. The measurements are repeated at intervals throughout the whole spectral region required, and from these results an absorption curve is drawn. This curve shows the position of the absorption bands, and it is

advisable to multiply the measurements near to the centres of these bands in order to determine as accurately as possible the wave-length for which the absorptive power is a maximum, this wave-length marking the centre of the band. As will readily be understood, the accuracy of the measurements depends upon two factors, first, the sensitivity of the recording instrument, and second, the determination of the wave-length of the energy, the absorptive power towards which is measured. In general it follows that the narrower the slit of the spectrometer the more homogeneous is the beam of rays falling on to the recording instrument, but it must also be remembered that the use of a narrow slit entails greater sensitivity in the recording instrument.

In the case of measurements of the absorptive power in the visible and ultra-violet regions, it is best to use a source of light which gives many rays of known wave-length closely situated together and not differing very much in their intensities. It might seem that the best source to use would be one giving a continuous spectrum, but it then becomes necessary to employ some method for the determination of wave-lengths. Except in certain special investigations, which will be referred to below, a source giving a complex line spectrum is always used.

Such a source is a spark between carbon electrodes, which are thoroughly impregnated with the oxides of molybdenum and uranium, as described by Jones. The two carbon rods, about 1 cm. in diameter, are filed to wedge-shaped edges, care being taken that the edge of the wedge is at right angles to the axis of the rod. These carbon wedges are boiled in a solution of uranium nitrate and then dried and heated to dull redness. This process is repeated three times. They are then boiled in a strong solution of ammonium molybdate and again heated to dull redness, this process also being repeated three times. In mounting these electrodes, just as in the case of the spark spectrum described above, the wedges are set parallel to one another, and to the axis of the collimator tube.

The electric spark between cadmium electrodes has been used by Hartley and by Purvis as a source for absorption spectra observations. Although the cadmium spectrum consists of only a few very bright lines, yet the region between these lines is filled with a continuous background, which serves extremely well for the observation of fine-line absorption. It must not be forgotten, however, that errors may be introduced if it happens that an absorption band lies very close to the position of one of the bright cadmium lines. For this reason, in dealing with fine-line absorption, it is advisable to use alternately two sources, the cadmium spark and one other, the second one being used merely for the purpose of finding whether any absorption lines are present at or close to the position occupied by the cadmium lines. Hartley has also used the spark between electrodes made of an alloy of cadmium, tin, lead, and bismuth, the metals being melted together in atomic proportions. This, however, does not seem to be so satisfactory as the spark between pure cadmium electrodes.

Another source which gives the most excellent

results is the spark between two nickel steel rods, and this has the advantage of giving a spectrum rich in lines to as far as $\lambda=2100 \text{ \AA}$.

The use of one of these sources which gives a spectrum of bright lines is manifestly superior to a source giving only a continuous spectrum, because the bright lines, being of known wave-lengths, serve as land-marks from which the wave-lengths of the absorption lines or bands may be measured.

Owing to the enormous multiplicity of the lines in the uranium and molybdenum coated carbon electrodes or nickel steel electrodes mentioned above, some difficulty may be found in recognising these lines and finding their wave-lengths. This spectrum may, however, easily be calibrated by photographing in juxtaposition to it a spectrum containing a few lines of known wave-length, as, for example, the cadmium spectrum. If the photograph then be measured with a travelling micrometer the whole of the spectrum can be calibrated with the help of Hartmann's formula already described. By matching this calibrated spectrum with the photograph of the same spectrum taken when the absorbing substance has been interposed, the limits of the absorption may at once be read off. Very frequently absorption spectrum measurements are expressed in wave-numbers and not in wave-lengths.

If it be desired to observe absorption bands or lines in the red and yellow regions of the spectrum, it will generally be found that emission spectra do not contain sufficient lines in these regions to justify their use for this purpose. Some other source must be sought for, and it has been found that very satisfactory results are obtained with interference fringes. These interference fringes are obtained simply enough by the use of the Edser and Butler interference apparatus described above. A source of light giving a continuous spectrum in the red and yellow is used, and by means of a condensing lens a slightly converging beam of light is thrown on to the interference plates, which are placed immediately in front of the slit of the spectro-scope. Since the wave-numbers of the fringes are very easily obtained they may readily be used for the observation of absorption bands.

Although for simple qualitative measurements of absorption in the visible region it may be sufficient to make visual measurements by means of a spectrometer, yet in any accurate work upon absorption it is necessary to determine the absorptive power of the substance investigated towards all the rays of the spectrum, visible and ultra-violet. In such work it is obvious that visual observation must give place to photographic methods. Hartley was the first to standardise the study of the absorption spectra of substances in the visible and ultra-violet regions, and it is to him that we are indebted for most valuable pioneer work in this field. The method he employed was in the main qualitative, and has now been almost entirely superseded by a quantitative method of measurement, which is very much more accurate in every way. Since the absorption spectra of some thousands of organic compounds observed by Hartley's method have been described in the literature it is necessary first to give a description of his procedure. In order to obtain the

position of maximum absorption corresponding to any absorption band the concentration of the absorbing substance is steadily decreased. It will be found that the absorption band or bands become narrower and narrower until they finally vanish. In this way the head of the absorption may be obtained, and this corresponds to the position of maximum absorption in the case of each band. It will be found most convenient to examine the absorption of a compound by dissolving it in some suitable solvent, when the molecular concentration may be decreased simply by lessening the thickness of the solution examined. For this purpose may be used an adjustable absorption cell as shown in Fig. 10, which consists of two glass tubes which fit loosely one inside the other. Both of these tubes are ground flat at one end and square to the axis, and have a quartz plate cemented in each case as shown at A and B. C is a bulb tube sealed to the side of the outer tube, and serves to take up the solution when the thickness of the layer is decreased by pushing in the inner tube. At D a broad india-rubber band is slipped over the junction in order to keep it water-tight, and this may be about 1 in. broad. The outer tube is about 1 in. wide and 6 ins. long, and it

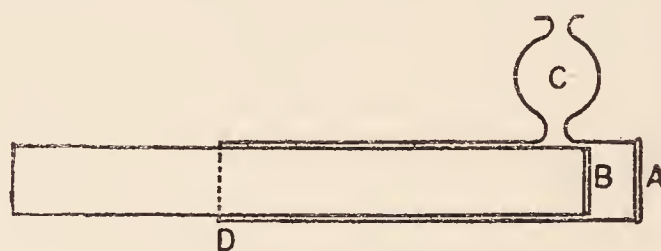


FIG. 10.

has a millimetre scale etched upon it, this scale being so ruled that its zero division coincides with the inner side of the quartz plate A, and thus the reading of the inner side of the plate B upon the scale gives the thickness of the solution. The inner tube is preferably lined with black paper, so as to stop as far as possible the reflection of light from the glass walls. In actual practice a solution of known strength of the substance in a suitable solvent is made of some standard strength, say $\frac{1}{10}$ th normal. This is then put into the cell which is adjusted so that the thickness of the layer is 30 mm., and a photograph is then taken of the source after passing through this thickness; the layer is then reduced to 25 mm., and a photograph again taken, this being repeated for the lengths 20, 15, 12, 10, 8, 6, 5, and 4 mm. If, as is most probable, the 4 mm. layer of the solution is not entirely diactinic, the solution is diluted ten times and the spectrum photographed through the same thicknesses as before. If necessary this may also be repeated for solutions of $N/1000$ and $N/10000$. Except in certain peculiar cases it will be found that there is no need to dilute beyond $N/10000$. The photographs thus obtained will give a complete record of the change of absorption to be observed in passing from 30 mm. of $N/10$ to 4 mm. of $N/10000$. If it be desired, of course, a normal solution of the substance may also be examined, though this in the case of organic compounds is very rarely necessary. The wave-lengths or wave-numbers of the absorption lines, or of the limits of the absorption bands, may be

read in the case of these photographs either by comparison with a calibrated photograph of the spectrum of the source or by interpolation between any standard lines in the spectrum. These wave-lengths or wave-numbers are plotted against the equivalent concentrations of the substance under examination. Hartley in his earlier papers used the equivalent volume of solution of a fixed quantity of the substance, and later an equivalent thickness of solution of fixed concentration. In the first case the effect of a given relative change in the amount of the substance was more marked at smaller than at greater concentrations, and in the second case exactly the opposite is true. If, however, the logarithms of the relative thicknesses be used, it will be seen that a given relative change in dilution or thickness will be represented by the same distance on the diagram, whatever be the actual strength of solution. In actual practice the logarithms of the relative thicknesses of the weakest solution used (in the above case $N/10000$) are put on the ordinates, and the measurements of the absorption limits on the

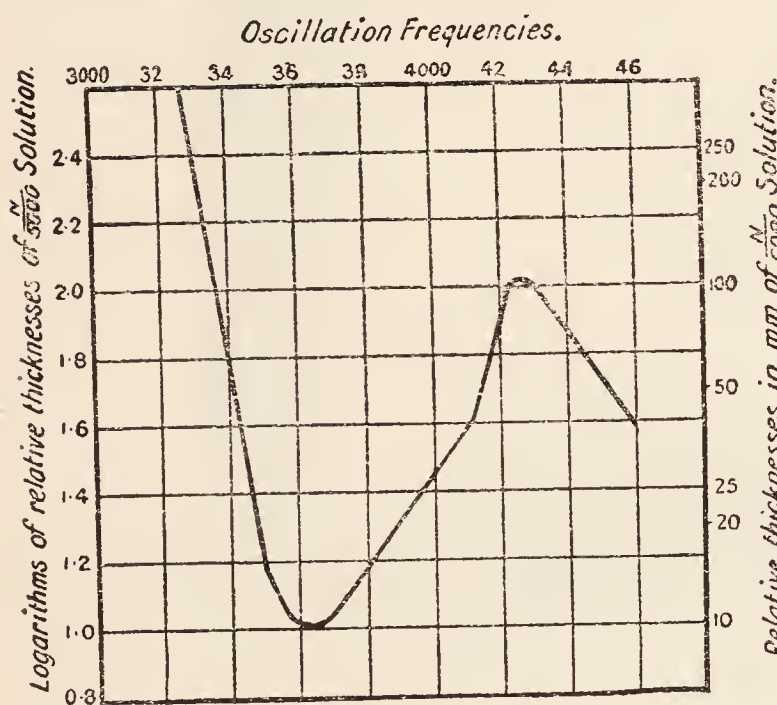


FIG. 11.

abscissæ, and the line drawn through the points so obtained gives the absorption curve of the substance under examination. Such an absorption curve is shown in Fig. 11, which represents the absorption of acetyl-acetone in alcoholic solution.

There are two objections to this method which are of some importance. In the first place the measurement of the absorptive power is only qualitative, and in the second place errors are very liable to occur, owing to the unequal intensity of the lines in the spectrum of the source employed. On the other hand, both these objections are surmounted by the use of the rotating sector photometer, by means of which accurate quantitative measurements of the absorptive power can be made at any wave-length between 6000 Å and 2100 Å. This instrument is shown in Fig. 12, and the principle involved is a very simple one. Two prismatic lenses are mounted vertically above one another, and are so adjusted that they focus two images of the source superimposed on the slit. In front of the slit is placed a bi-prism, with the result that two spectra are obtained in juxtaposition and of the same intensity. In the path

of each light beam is interposed a rotating sector, and if both sectors have equal apertures and rotate with equal speed the amount of light in each spectrum is the same. The lower sector has a fixed aperture, whilst the aperture of the upper sector can be adjusted to any desired size. The cell containing the absorbing substance is placed in the path of the lower beam of light, when, of course, the intensity of certain rays will be decreased. The aperture of the upper sector is reduced in size by a fixed amount and a photograph taken of the two spectra. On this photograph will be seen one or two points at which the two spectra have equal intensities.

The wave-length at these points is determined, and at these wave-lengths the absorptive power is given by the ratio of the two sector apertures. Absorptive power is usually expressed in terms of the extinction coefficient, which will be dealt with below. If the aperture of the lower sector is called 100 and that of the upper sector be 50, then the extinction coefficient is given by $\log 100/50 = 0.30103$. In actual practice it is possible to take many photographs on the same plate, a different aperture of the upper sector being used for each. The most convenient apertures, assuming the full aperture to be 100, are 60, 50, 40, 30, 25, 20, 15, 12, 8, 6, 5, 4, 3, 2, 1.3, 1, and it will be found advisable to increase the exposure as the aperture is decreased, in order that the density of the photograph of the upper spectrum is kept constant. This is secured by making the exposure time inversely proportional to the aperture of the upper sector.

It is most convenient to express the absorptive power in terms of the molecular extinction coefficient, which is given by $\log 100/A \times 1/cd$, where A is the aperture of the upper sector on the above scale, c is the concentration in gram-molecules per litre, and d is the thickness in cms. of the absorbing layer. It is only possible in this way to compare together the absorptive powers of different substances. Fig. 13 shows the absorption curve obtained with pyridine in alcoholic solution.

As will be shown later, the influence of a solvent upon the absorption exerted by a substance is often very marked, and it may prove of importance to observe the absorption of the substance in the absence of any solvent. This may either be done with the substance in the state of vapour or in the liquid state. Hartley and Purvis have both examined the absorption of the vapours of a number of organic substances, and the method adopted was as follows: A glass tube about 2 cms. wide and 20 cms. long, with quartz plates fastened at each end, is filled with the vapour of the substance by aspirating a current of air previously saturated with the vapour by bubbling it through the substance contained in a small wash bottle.

Since this method does not easily allow the concentration of the substance to be changed, which is necessary in order to obtain the complete absorption curve, a similar tube made of quartz with the ends sealed on may be substituted. To this quartz tube is attached a side tube connected with a small flask containing the substance, and the whole apparatus is exhausted to the highest possible point. The bulb containing the substance is now heated to certain known temperatures at each of which a

photograph is taken, this being continued until sufficient concentration is reached. It must be remembered that in order to guard against any condensation of the substance in the quartz absorption tube this must be kept at a constant temperature, which is at least 30° higher than

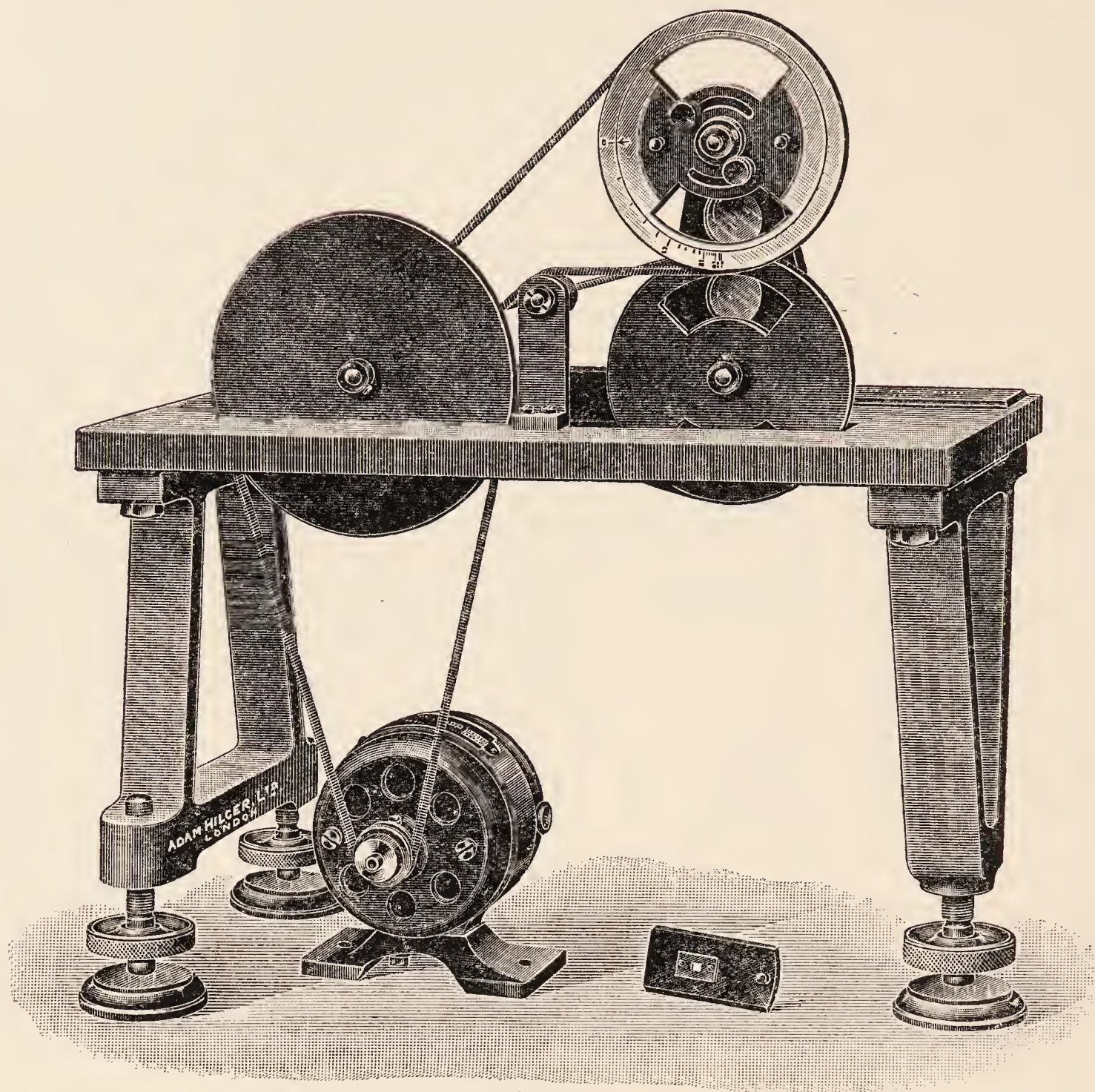


FIG. 12.

the highest temperature to which the substance is to be heated. The concentration of the substance in the quartz absorption tube may readily be calculated from the vapour pressure curve of the substance under investigation. These observations will give a complete record of the absorption of the substance similar to that obtained for solutions, and from which the absorption curve may be drawn.

This apparatus is too large to use with the sector photometer described above, and if it be required to obtain quantitative measurements of the absorptive power of a vapour the photometer must be so designed as to admit the use of a long absorption cell. This type of measurement, however, is rarely required, the problem most usually consisting of the measurement of the detailed structure of the absorption bands shown by many gases and vapours. As a general rule, substances in the liquid state or in solution exhibit broad absorption bands of the type shown in Fig. 13. When certain substances are examined in the state of vapour it is found that the broad absorption band can be resolved into a series of sub-groups, and, further, that each sub-group can be resolved

into a series of fine absorption lines. The accurate measurement of these absorption lines

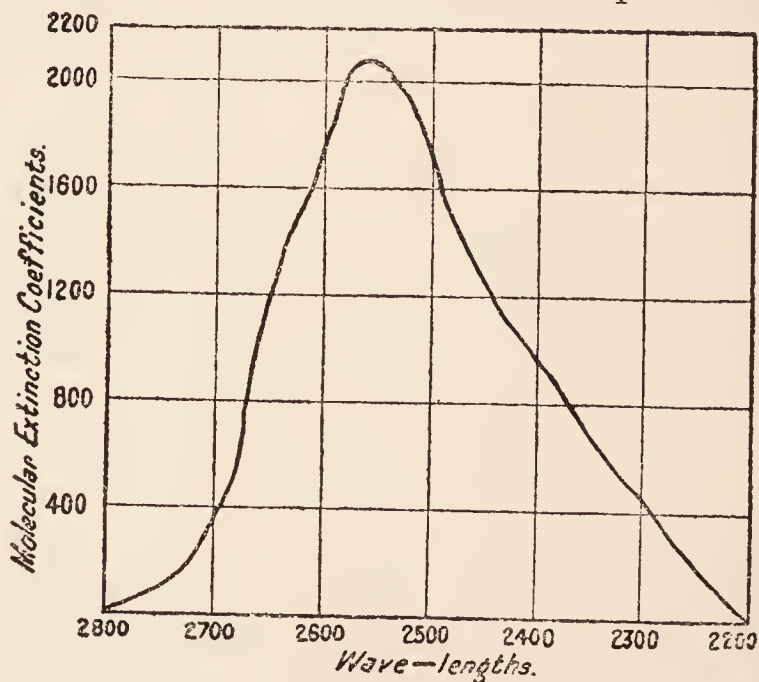


FIG. 13.

constitutes a very important branch of spectroscopy, and as the method of investigation differs from that already described, this may be

mentioned. The essential point is that a source of light giving a continuous spectrum must be used, as otherwise some of the absorption lines will be obscured. For observations in the visible and near ultra-violet regions a pointolite or a 1/2 Watt lamp may be used, but the emission does not extend far into the ultra-violet. For investigation of the region beyond $\lambda=3500$ Å it is advisable to use as source the spark between aluminium poles under water. A powerful condensed discharge must be used in series with a spark gap in air, and, further, the spark length between the aluminium poles must be adjusted with considerable care by means of a micrometer screw.

Obviously, some means of wave-length determination must be at hand, and for this purpose some known emission spectrum is photographed alongside of each absorption spectrum. The wave-lengths of the absorption lines can be measured by interpolation between those of known lines in the standard spectrum by the use of Hartman's formula.

The measurement of the absorptive power of homogeneous liquids presents considerable difficulty, owing to the necessity for using in the great majority of cases exceedingly thin films. Owing to the great viscosity exhibited by very thin liquid films it is very far from easy to obtain sufficiently thin films of known thickness for purposes of absorption spectra. The best method is to press together two accurately worked quartz plates with a small quantity of the liquid between them, and then to measure the thickness by means of a spherometer.

VII. Application of spectroscopic methods to analysis. Spectroscopic methods have found considerable application in many directions. Although in most cases the use of the spectroscope is restricted to the qualitative analysis of substances, yet it has been found possible to develop certain systems of quantitative analysis by its means. These applications may conveniently be treated under the three headings of emission spectra (flame, arc, and spark), phosphorescence, and absorption.

(a) *Emission spectra. Qualitative analysis.*—Although in the qualitative spectrum analysis of a substance some knowledge may be gained if the substance give a flame spectrum, yet for complete analysis by the spectroscope recourse must be had to the arc or the spark as a means of illumination, preferably the latter.

In general, owing to its wider application, the spark spectrum is most suited to a qualitative analysis of substances, because they are more often sufficiently good conductors for the high potential current of a spark discharge. Then, again, arc spectra are not possible in the case of solutions. In dealing with solid substances such as, for example, native minerals, it will be found perfectly possible to obtain the spark discharge between fragments of such minerals. These small fragments may be attached by means of fine platinum wire to iron or steel wires, or may be held in small clips which are mounted in any convenient form of sparking apparatus by means of which the spark length can be varied.

In dealing with the spark spectra of solutions it is important that the solution be made the negative pole, and it is most convenient to use an

induction coil giving a 2 or 3 in. spark in air. A considerable advantage is often gained by comparing the spectra given by the spark with or without a condenser. When no condenser is used it will be found that the spectrum shows the bands of nitrogen. The solutions of the chlorides of the alkaline earths, metals, and of certain rare earths show with the non-condensed spark, spectra of bands and lines. This is also true for chromium, iron, lead, bismuth, mercury, copper, silver, and gold. The chlorides of the alkalis, tin, antimony, zinc, cadmium, thallium, iridium, gallium, nickel, cobalt, and the platinum family give line spectra. The condensed spark gives almost entirely line spectra, but superposed on these will be the line spectra of air, platinum, and sometimes of chlorine. Considerable differences are often obtained between the spectra given by the spark with or without a condenser, and the unequal sensitiveness of the spectra often affords decided advantages. It is possible for this reason to detect the presence or the absence of various substances in very complex mixtures, which with the condensed spark give such complicated spectra as to make the individual lines very difficult to pick out.

On this account it is sometimes very useful to use a condenser, the capacity of which can be varied at will. Such a condenser can easily be made out of two glass tubes, one of which is sufficiently smaller than the other, as to slide easily in and out. The larger tube may be about 2 ins. in diameter, and both the tubes are coated on the outside with tin-foil. It is advisable to have a wooden handle fitted to the inner tube, so that it can be moved without danger of touching the coatings with the fingers, and also to have the ends of the wider tube expanded a little, so as to guard against any damage to the inner coating when it is moved in or out.

It has been shown by de Gramont that if the condensed spark discharge be passed between fragments of minerals the spectrum shows bright emission lines, not only of their metallic components, but also of the non-metallic components in a number of cases, as, for example, chlorine, iodine, sulphur, phosphorus, arsenic, and antimony in the case of antimonates and thio-antimonates. In the spark spectrum of no mineral up to the present time have the lines of oxygen and fluorine been noted. We are indebted to de Gramont for an exhaustive study of this method of qualitative analysis of many minerals.

Among the conclusions drawn by de Gramont from his work may be mentioned the following: Those elements which are present only in very small quantities are easily detected. If the condenser is not used the spectra of the non-metals disappear and the metals themselves only show the brightest of the lines. Those minerals which are not good conductors but which are volatile in the spark give equally good results. Fused salts also show the spark spectra both of their metallic and non-metallic elements.

It has been shown by Urbain that minerals such as blende can be analysed spectrographically, using the electric arc. In one case he analysed 64 different samples of blende, and was able to detect quite easily the presence of germanium, gallium, and indium.

It is well known that the arc and spark

spectra of the same element frequently differ very considerably. There have been found lines in the latter which are not present in the former, and to these Lockyer has given the name of enhanced lines. On the other hand, the flame spectrum, as a general rule, is much simpler than that of the arc spectrum, this being attributed to the fact that the temperature of the flame is lower than that of the arc. Again, each particular type of spectrum, whether flame, arc, or spark, is very sensitive to change in the exciting cause, especially is this true in the case of spark spectra, where the relative intensity of the lines is found to change very markedly when the capacity of the condenser or the amount of self-induction in the circuit is varied. It will be evident, therefore, that in such work as quantitative spectrographic analysis great care must be taken to keep the conditions constant throughout the whole series of experiments.

Detection of mercury in explosives.—The basis of this method is the electrolysis of a properly prepared solution of the explosive, using a platinum wire as cathode. The platinum wire is then put into a vacuum tube and gently heated, when the mercury may at once be detected by its characteristic spectrum. If the explosive is completely soluble in the ordinary solvents, ether, alcohol, or acetone, 2 grms. of an average sample are dissolved in a suitable solvent and a sufficient quantity of sulphuric or hydrochloric acid is added to give a faintly acid reaction, and the solution is then electrolysed. If the explosive is only partially soluble 2 grms. are first extracted by decantation, the residue is then dried at a low temperature and evaporated with strong nitric acid to destroy all organic matter. It is then taken up with very dilute hydrochloric acid and electrolysed. The solution in the organic solvent is also electrolysed. Since the test for mercury is exceedingly delicate great care must be taken to avoid any contamination during the process of extraction and solution. It is best to use the same dish for solution and for electrolysis.

The electrodes are made of platinum wire 0.015–0.02 in. in diameter and 1 in. long. The dish is nearly filled and is carefully covered with glass or cardboard, the electrodes being passed through this cover. A current of 2 ampères at 10 volts is used, and may be continued all night. The cathode is then taken and carefully dried and dropped into the vacuum tube. This tube is about $2\frac{1}{2}$ ins. long by $\frac{1}{8}$ in. in bore. A platinum wire $\frac{1}{2}$ in. long is sealed in at one end, and the other end is drawn out ready for scaling, but leaving sufficient room to allow the entrance of the cathode. The second electrode also is a platinum wire $\frac{1}{2}$ in. long, and sealed in a small side tube. After exhaustion the tube is sealed off and the current from an induction coil passed through it. It is then gently heated, and the presence of mercury is at once recognised by the green line at 5461 Ångström, and also by the two yellow lines at 5791 and 5760 Ångström.

By this method the presence of as little as 0.000001–0.0000001 gm. of mercury may be detected.

The same piece of platinum wire must never be used twice, for it has been found impossible to remove the mercury by the action of heat

so that it will not still continue to give the mercury spectrum in a vacuum tube. The amount of mercury present may be estimated quantitatively by placing the cathode in a test tube with a small quantity of iodine and gently heating it. The mercury is converted into mercuric iodide, which then may be treated in any convenient manner.

Quantitative analysis.—Hartley has shown, in the first place, that the spark spectra of solutions of metallic salts show the lines of the metallic radicle, and, further, that the effect of diluting these solutions is first to weaken these lines and then to shorten them until they finally disappear. It has been found on further investigation that all the lines of a metal do not disappear at the same dilution, and further that, given the same conditions, the same lines always disappear at the same dilution. These investigations have been continued by Pollok and Leonard and by de Gramont, and the name of residual or ultimate lines has been given to those lines which persist the longest when the substance is diluted. The method adopted by Pollok, which is based on Hartley's investigations, is to use gold electrodes and to compare the photographs of the spectra given with a 10 p.c., 1 p.c., 0.1 p.c., 0.01 p.c., and 0.001 p.c. solution of a metallic salt. In taking any photograph the spectrum of the spark between the gold electrodes alone is photographed, using a long slit; then the length of the slit is shortened and the spark spectrum of the particular solution required is photographed without moving the photographic plate. In this way the gold lines may at once be recognised. By comparing the photographs taken at various dilutions of the salt the relative persistence of the various rays is obtained. The most persistent, that is to say, the residual lines, have not necessarily any connection with their intensity. It is evident that in the spectroscopic examination for the presence of traces of any element it is by these residual rays that an element may be recognised when present in very small quantities. Inasmuch as it is quite possible, and has indeed been done in very many cases, to determine the dilutions at which the various lines disappear, it may be seen that we have herein a quantitative method of spectrum analysis.

When photographs of the various dilutions of the solution of a particular metal have been taken, the next step is to observe the lines of that metal, which appear at each particular dilution. For the sake of convenience, Hartley indicates the persistence of the various lines by means of the letters of the Greek alphabet in the following way. By ω lines only seen in a 0.001 p.c. solution, by ψ those seen in a 0.01 p.c. solution and not in a 0.001 p.c. solution, by χ those lines seen in a 0.1 p.c. solution but not in a 0.01 p.c. solution, and by ϕ those seen in a 1 p.c. solution but not in a 0.1 p.c. solution, then by σ those seen in a strong solution and not in a 1 p.c. solution, whilst by τ he denotes those lines which are seen in the metallic spark, but not in any solution.

In actual analysis, therefore, it is only necessary to compare the spectrum photographs taken of the unknown solution with the photographs of the particular metals in the various dilutions, whence the percentage of each par-

ticular metal in the substance under examination may be arrived at.

It is hardly necessary to point out that in every photograph the conditions of exposure must be the same, and also in examining the solutions that exactly similar apparatus and electrodes be employed.

The apparatus recommended by Pollok for this particular purpose has already been described in the section dealing with spark spectra. A condenser should be used, and if it be desired to remove the air lines a self-induction coil may also be inserted.

As a result of the method described above the gold lines may be easily recognised, and the wave-length of the other metallic lines may be obtained by interpolation between the gold lines, using either an interpolation formula or an interpolation curve.

A very large number of these quantitative observations have been made by Pollok, by Leonard, and by de Gramont on the spectral estimation of the elements. These observations have been collected together and published in Twyman's Wave Length Tables.

This method can be applied to the quantitative analysis of minerals and alloys; for example, de Gramont has shown that it is possible to estimate by this method the silver in specimens of galena.

Hartley describes the application of this method to the quantitative analysis of alloys; for example, old and rare coins, which, as he points out, saves the cutting and destruction of the coin. He checked his results by making an alloy of the same composition as the coin as found by the spectrographic method, and proved that the spectra of the two were in every way identical. In one case he found 13.96 p.c. of lead, 72.35 p.c. of copper, 12.70 p.c. of zinc, and 0.85 p.c. of iron. He afterwards found that these figures were correct by the ordinary methods of chemical analysis.

Methods have been devised for the quantitative estimation of lithium, sodium, and potassium depending on the persistence of the characteristic lines in the flame spectrum of these elements. For example, Ballman found that if a solution of lithium chloride be diluted until the lithium line ($\lambda=6708 \text{ \AA}$) disappears, then there is contained in every 3345 c.c. of the solution 0.001 gr. of the lithium salt.

Mottram has devised a method of quantitative estimation of potassium and sodium, which he applies to the analysis of animal tissues and blood. He uses a direct-vision spectroscope, with a fixed slit in front of which a piece of cobalt glass is fixed. A Bunsen burner is used, guarded with a blackened metal cylinder having a hole in one side through which the flame is viewed and a slit through which a platinum spoon can be introduced. This Bunsen burner is provided with a platinum gauze nozzle, and in order to keep the gas pressure constant a toluol manometer is used for measuring the pressure and a gas tap with a long arm attached for delicate adjustments. The following precautions were found necessary. The distance at which the spectroscope and cobalt glass is fixed in front of the metal cylinder surrounding the flame must always be the same. The position of the spoon in the flame must be

constant, and in Mottram's experiments it was so placed that the bottom of the spoon was just above the apex of the blue inner zone of the flame. The gas pressure was kept very constant as measured by the difference in heights of the toluol columns in the manometer (0.3 cm.). The amount of diffused light in the room must be small and constant. It is best to carry out the experiments in a dark room lighted by an 8 candle-power electric lamp. The spectroscope must always be directed to the same part of the flame; it was directed above the spoon so that the continuous spectrum produced by the incandescent spoon was just invisible. The first definite observations should be postponed until the eyes become accustomed to the dull light of the room (about half an hour). The method for the estimation of sodium depends on the fact that different quantities of sodium sulphate when placed on the spoon and introduced into the flame take different lengths of time to burn off, the time being proportional to the amount. Mottram recommends the use in this case of a second cobalt glass. When the platinum spoon has been cleaned with strong hydrochloric acid and the blow-pipe until the D line can no longer be seen through the two cobalt glasses, 0.02 c.c. of the solution under examination containing a known weight of the substance in which it is required to estimate the sodium is placed in the spoon. The D line, which at first is clearly seen, gradually fades until it disappears. The time is then noted, and this time is compared with a table which has been previously prepared when known weights of sodium sulphate were placed on the spoon under identical conditions. From this the percentage of sodium can be estimated.

Mottram gives a table showing the times taken by known quantities of sodium, which vary from $6\frac{1}{2}$ minutes with 0.000001 gr. of sodium to 13 minutes at 0.000003 gr.

The estimation of potassium depends upon the least amount of potassium sulphate that will give the red potassium line ($\lambda=7699.3 \text{ \AA}$). In Mottram's apparatus this amount was 0.0000002 gr. Only one cobalt glass was used in this case, and just as before 0.02 c.c. of the solution is placed in the spoon. If the potassium line is then seen, the solution is diluted and again examined, this being continued until the line just becomes invisible. This dilution corresponds, therefore, to 0.0000002 gr. of potassium in 0.02 c.c. of solution.

In the application of this method to the estimation of sodium and potassium in animal tissues and in blood, owing to the fact that carbon and acid radicles other than sulphate materially alter the constancy of the results, great care must be taken in these cases to destroy all carbonaceous matter and to ensure that the sodium or potassium is only present as sulphate.

Phosphorescent spectra.—Among the many substances which show phosphorescence under the influence of cathode streams perhaps the most interesting are the rare earths. This phenomenon has been frequently used as a means of testing the progress of the fractional separation of the rare earths from one another. Much of this work was based on the

assumption that the phosphorescent spectrum is a characteristic property of each rare earth. This, however, is not the case, because it has been proved by Leonard and Klatt and by Urbain and his pupils that phosphorescence is a phenomenon characteristic of mixtures of two or more substances. No rare earth gives any phosphorescence when it is pure, and indeed it would seem that no pure substance whatsoever can phosphoresce. Urbain has shown that phosphorescence is a property of diluted matter, and that in order to obtain the phosphorescence of a substance it is necessary that it be mixed with a large quantity of some diluent. To the active principle of such mixtures has been given the name of phosphorogene, and for every pair of substances, phosphorogene and diluent, there is one definite mixture which gives an optimum of phosphorescence. On either side of this optimum, that is if the phosphorogene be either increased or decreased, the phosphorescence is weakened. Moreover, a phosphorescent spectrum as a rule contains several bands, and there is an optimum condition for each of these bands; also these conditions are not the same for all the bands in any one spectrum. It may happen that as the quantity of phosphorogene is increased in a given mixture the conditions are successively arrived at for giving the optimum for each of the bands in turn, with the result that the colour of the phosphorescence appears to the eye materially to alter. Generally speaking, the optimum condition corresponds to the presence of a very small quantity of the phosphorogene. It will be understood from this that the variations in the phosphorescence observed during the fractional separation of the rare earths, will be very varied as the optimum condition for each of the phosphorogenes present is passed. The extraordinary variations which can be obtained in the relative intensity of the various bands in any one phosphorescent spectrum explain why it has been thought by some people that each separate band is the characteristic spectrum of a single element.

Urbain's investigations have proved conclusively that this theory is completely untenable, and they also show the great care that must be exercised in the interpretation of any phosphorescent spectrum that is observed. At the same time, in the fractional separation of the rare earths, owing to the very small differences in their atomic weights, it is necessary to use some physico-chemical observations (such as spectroscopic) to characterise the elements.

In this connection may be used emission, absorption, and phosphorescent spectra, all three of which are given by the rare earths.

In carrying out any fractional separation on the rare earths, if the order number of the fraction is made the abscissa and the atomic weight the ordinate, the curve drawn through these points at the beginning of the fractionation will of course appear continuous and regular. As the fractionation advances the curves will begin to give indications of horizontal steps, which become more marked as the process is continued. These steps, as a rule, correspond to the existence of pure substance. They may, however, be mixtures similar to constant boiling mixtures in a distillation. It is evident from

what has been said above, if these horizontal steps give any evidence of phosphorescence that they must correspond to a mixture, and that if they correspond to single pure substances they will not phosphoresce.

It will be seen, therefore, that although phosphorescence cannot be utilised as a test for the purity of a substance, yet it may within certain limits be of great value for the characterisation of an element. But for the complete identification of such an element it is necessary also to make use of its emission and absorption spectra.

Absorption spectra.—Perhaps it may not be out of place before dealing with specific absorption spectra observations to define the limits of transmission of the various materials which are used in different branches of spectroscopy.

Substance	Transmits all rays between	
Heavy flint glass . . .	2 μ	and 0.3500 μ
Flint glass . . .	2 μ	and 0.3300 μ
Crown glass . . .	2 μ	and 0.3200 μ
Light crown glass . . .	2 μ	and 0.3000 μ
Quartz . . .	4 μ	and 0.2000 μ
Calcite . . .	2.2 μ	and 0.2150 μ
Fluorite . . .	7.6 μ	and 0.1230 μ
Rock salt . . .	18 μ	and 0.2000 μ

Frequently in constructing spectroscopes it is necessary to make use of a reflecting mirror of some kind. It may be pointed out that a silvered surface has very poor reflecting power in the ultra-violet region. The maximum of transmission by a silver layer lies between 3360 and 3100 Ångströms, and such a layer consequently cannot reflect light of this wavelength. A speculum metal surface, however, seems to have the power of reflecting ultra-violet light down to the shortest wave-length yet observed. Similarly a nickelled surface has excellent reflecting power in the ultra-violet region. Nickelled mirrors may easily be obtained by exposing the surface to be coated to the cathode streams from a nickel cathode in a high vacuum.

Absorption of the oxides of nitrogen and ozone in the infra-red and their quantitative estimation.—Warburg and Leithäuser have measured the absorption of N₂O₅, NO₂, N₂O₄, NO, N₂O, and O₃ in the infra-red, and find that all these gases exhibit very well marked and characteristic absorption bands between the limits 2.7 μ and 7 μ .

The apparatus used was a fixed arm spectrometer with a single fluorite prism. The source of illumination was a Nernst lamp, and the absorption bands were detected by means of a vacuum bolometer, whilst the wave-lengths of the absorption bands were calculated from the known dispersion curve of fluorite.

In the following table are given the wave-lengths of the absorption bands, in each case the most important band being marked in heavy figures:—

Substance	Absorption maxima in μ						
N ₂ O ₅ . . .	2.73	2.83	3.33	3.86	4.27	4.81	5.81
N ₂ O ₄ . . .	5.695						
NO ₂ . . .	3.38	6.11					
NO . . .	5.24	5.40					
N ₂ O . . .	2.79	3.54	3.86	4.02	(4.29)	4.45	
O ₃ . . .	4.74						

The absorption of these gases can be utilised for the quantitative analysis of the gas mixtures which contain one or more of these gases, provided that their quantities are not too great. A 30-cm. long absorption tube is used, and it is necessary to determine the intensity of the absorption band in each case corresponding to definite percentages of the gas in question. These percentages should be so small that the partial pressure of the gas lies between 0.3 and 1 mm. When these relations between intensity, and absorption and partial pressure of the absorbing substance have been determined for all the above gases the estimation of the amounts present in any given gas mixtures may readily be found.

Absorption spectra of nitrogen peroxide in the visible region and its estimation thereby.—Nitrogen peroxide, as is well known, exhibits a very characteristic absorption spectrum, which consists of a large number of fine lines in the visible region and a general absorption in the violet. Robertson and Napper have utilised this absorption for the quantitative estimation of small quantities of nitrogen peroxide in air or carbon dioxide. The absorption spectrum was photographed in each case with a spectrograph having a single dense flint-glass prism. A Welsbach incandescent mantle was used as a source of light, and the absorption vessel was a glass tube 40 cms. long with the ends closed by glass discs which were attached by cement. The estimation of the nitrogen peroxide in any gas is done by comparison of the photographs taken of the absorption exerted by the gas, with a series of photographs of the absorption spectra of carbon dioxide or air containing known definite amounts of nitrogen peroxide. It was found possible to estimate quantitatively an amount of nitrogen peroxide as low as 0.05 p.c. within 0.02 p.c. In the case of greater concentrations of nitrogen peroxide the accuracy is about 0.05 p.c.

Quantitative estimation of the nitrogen evolved in the decomposition of gun-cotton and nitroglycerin.—The above described method for the estimation of nitrogen peroxide has been applied to the Will test of decomposing gun-cotton and nitroglycerin.

The most satisfactory results in the case of gun-cotton, and also of nitroglycerin, were obtained by heating the substance in a measured current of pure carbon dioxide, and passing the gases through an absorption spectrum vessel as described above, and afterwards through a tube containing copper heated to redness. The gases from this decomposition tube were passed into potassium hydroxide solution and the total nitrogen measured. In the case of gun-cotton 2½ grms. are heated in an oil-bath to 135°, and a stream of specially pure carbon dioxide is passed at the rate of 1 litre per hour (controlled by observing the number of bubbles per minute in a small glass washing bottle containing sulphuric acid) through the vessel containing the nitrocellulose. The current of carbon dioxide containing the gases resulting from the decomposition of the nitrocellulose is passed through the absorption spectrum tube and the spectrum photographed at intervals of a quarter of an hour. The gases are then passed through a combustion tube con-

taining two spirals of reduced copper gauze and layers of Kreusler's copper oxide asbestos and reduced copper asbestos. The oxides of nitrogen are thereby reduced to nitrogen and the organic gases oxidised to carbon dioxide. The gas is then passed through a measuring burette containing strong caustic potash, and the volume of nitrogen is read at intervals. A curve is constructed showing the amount of nitrogen peroxide and of nitrogen evolved each quarter of an hour, and the character and slope of the curve is a measure of the stability of the sample.

Since certain preliminary experiments proved that water vapour has no influence upon the absorption spectrum of nitrogen peroxide, whilst the presence of liquid water causes a rapid absorption of this gas, great care must be

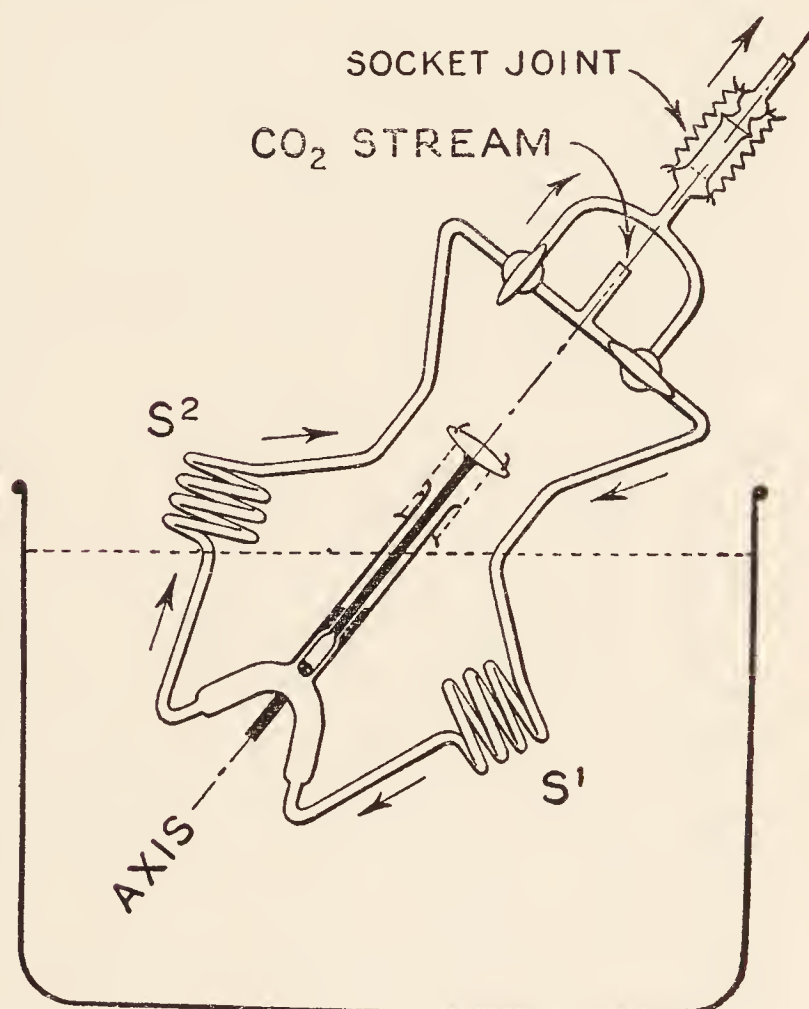


FIG. 14.

taken not to allow any water to condense in the apparatus. It was found that about 40 p.c. of the nitrogen evolved by the gun-cotton is in the form of nitrogen peroxide.

In the case of nitroglycerin, Jena glass-wool soaked in 0.3–0.5 grm. of nitroglycerin is placed in a horse-shoe shaped tube; this is closed by a stopper, which is greased and mercury-sealed. To each end of the horse-shoe is connected a spiral tube s^1 and s^2 in Fig. 14. The current of carbon dioxide may be passed down the right-hand spiral through the glass-wool and up the other spiral or *vice versa*, according to the way the three-way cocks are turned. The whole apparatus can be rotated round the axis, and, when starting, the spiral s^1 is immersed in an oil-bath of known temperature, and so the carbon dioxide receives a previous heating before it reaches the nitroglycerin. Spiral s^2 is protected by an asbestos sheet from the heat of the oil-bath, and is cooled by an air blast. Any volatilised nitroglycerin is condensed in this spiral. After a reasonable time has elapsed the

apparatus is rotated through 180° . The two spirals now exchange their functions, and any nitroglycerin in s^1 is restored to the system. The gases are then passed, as described above, first through the absorption spectrum tube and then through the heated tube of copper and copper oxide. In order to guard against any presence of nitroglycerin in the gases they are made to pass through a worm cooled with ice immediately on leaving the decomposition apparatus. As in the case of gun-cotton, described above, the current of carbon dioxide passes at a measured rate and the nitrogen peroxide is spectroscopically estimated by the method described for that substance.

The decomposition of nitroglycerin was studied between the temperatures of 90° and 135° , and it was found that this decomposition proceeds in as uniform a manner as that of a stable gun-cotton. Further, the whole of the nitrogen is evolved as nitrogen peroxide. Between 95° and 125° the rate of decomposition is a function of the temperature, and is doubled for every increase of 5° .

VIII. Spectrophotometry. In dealing with the quantitative analysis of substances which exhibit absorption two general methods may be employed. Firstly, the amount of an absorbing substance present in any given mixture may be determined by taking a photograph of the absorption exerted by the mixture, and comparing this with a series of standard photographs which have been taken of the absorption of the same substance at certain definite and known concentrations. That standard which exactly matches the absorption given by the unknown mixture will, of course, give the concentration of the absorbing substance in that mixture.

An example of this method has already been given above in connection with the estimation of nitrogen peroxide in the gases evolved on heating gun-cotton and nitroglycerin. It is manifest that exactly the same principle may be applied to substances in solution, provided that standard absorption records can be obtained of known concentrations of the same substance in the same solvent.

In the second method the amount of absorption exerted by the substance in a given mixture is determined quantitatively by means of a spectrophotometer, these observations being made at that region of the spectrum where the characteristic absorption by the substance occurs.

Before giving an account of the instruments and methods employed, a few words may be said about the laws of absorption and their application to quantitative analysis.

If light of intensity I enters an absorbent medium having a thickness equal to 1, the light which emerges will be reduced to $1/n$, and after passing through a second layer of equal thickness the intensity will be reduced to $1/n^2$. If the thickness of the layer be denoted by d , the intensity of the light will be reduced to $1/n^d$. From this it may be seen that as the thickness of the layer increases in arithmetical progression, the transmitted light will decrease in geometrical progression.

If, therefore, the intensity of the incident light be put equal to I and dI be the amount

lost during its passage through a layer of thickness dx , we have $dI = -kI dx$.

If we integrate between the limits $x=0$, when the intensity of the incident light $=I_0$ and $x=d$, when the intensity is I , then it will follow that

$$I = I_0 e^{-kd} \quad (1)$$

where k is a constant depending on the absorbing medium and the wave-length of the light, and e is the base of natural logarithms.

Usually e^{-k} is denoted by the symbol a , and is known as the absorption coefficient, so that we may write

$$I = I_0 a^d \quad (2)$$

and if $d=1$, we have $a = I/I_0$, so that a represents the fraction of the light which is transmitted by a layer of thickness 1. This relation is known as Lambert's law. Bunsen and Roscoe expressed the absorption power of a given region of the spectrum in terms of the 'coefficient of extinction,' and defined this as the reciprocal of that thickness which causes the reduction in intensity of the light to $\frac{1}{10}$ th of its original value. If this coefficient of extinction be expressed by α then, when in equation (2) $I/I_0 = \frac{1}{10}$, $d = \alpha$, therefore $a^\alpha = \frac{1}{10}$, whence $a = 10^{-1/\alpha}$.

Substituting this in the general equation (1) we have $I = I_0 10^{-\alpha d}$, whence $\alpha = \log I_0/I \times 1/d$. In order to compare the relative absorptive powers of substances it is necessary to take the molecular concentration into account, and the usual practice is to express all measurements in terms of the molecular extinction coefficient, $M.E. = \log I_0/I \times 1/cd$, where c is the concentration in gram-molecules per litre and d is the thickness in cms. of the absorbing layer.

In order to apply this to the quantitative estimation of absorbing substances we make use of the relation known as Vierordt's absorption ratio. According to Beer's law the absorption of a given solution is inversely proportional to the concentration, that is, if the absorption were observed of a given thickness of a solution of concentration c , the same absorption would be exhibited by half that thickness of a solution of concentration $2c$.

It follows, therefore, that in solutions of different strengths of the same substance the extinction coefficient is proportional to the concentration c .

If the concentrations of a series of solutions of the same substance be expressed by c, c_1, c_2, \dots and the corresponding coefficient of extinction by a, a_1, a_2, \dots , then it follows that $\frac{c}{a} = \frac{c_1}{a_1} = \frac{c_2}{a_2} = A$. From this we have generally $c = aA$, when A is called the absorption ratio. A may be determined once for all for any substance in the given solvent, and the concentration of a solution of the same substance in that solvent may at once be determined by finding the extinction coefficient and substituting it in the formula $c = aA$.

It must be remembered, of course, that the above relation is only true for any one wave-length.

It is evident also that the above relation only holds good when a single absorbing substance is examined in a non-absorbing solvent, and that if two absorbing substances are present,

such as occur when the solvent exerts absorption, or when two absorbing substances are dissolved in a diastinic solvent, the observations become a little more complicated. It is necessary in such a case to determine the extinction coefficient for light of two different wave-lengths. If, for example, we have a solution of two coloured substances of unknown concentration, x and y respectively, it is necessary to determine the extinction coefficient for two different parts of the spectrum. Let these be α and α_1 respectively. Then if A and A_1 and B and B_1 be the absorption ratios for the two substances at the two different wave-lengths, it follows that

$$a = \frac{x}{A} + \frac{y}{B} \text{ and } a_1 = \frac{x}{A_1} + \frac{y}{B_1}.$$

Solving these two simultaneous equations we get $x = \frac{AA_1(\alpha B - \alpha_2 B_1)}{A_1 B - A B_1}$ and $y = \frac{BB_1(\alpha A - \alpha_1 A_1)}{A B_1 - A_1 B}$ from which, of course, the concentrations of the two substances may at once be calculated.

The measurements of the amount of light absorbed by or transmitted through substances such as are required for the determination of the extinction coefficient are made with a spectrophotometer, which is an instrument by means of which the relative intensities of two different beams of light may be compared at any required wave-length in the visible spectrum.

The Vierordt instrument consists in the main of an ordinary spectrometer, the slit of which is divided into two, an upper and a lower portion, which are provided with separate micrometer screws for adjusting the width. If both halves of the slit are set at equal width, and are illuminated with a beam of white light, and in front of one half is placed the absorbing material, there will be seen in the eye-piece two spectra, one above the other, one of which is less intense owing to the absorption which has taken place. The difference in intensity between the two spectra at any given wave-length may be determined at once by decreasing the width of the half of the slit corresponding to the brighter spectrum until the two appear equal in the field of view of the telescope. If the original widths of the slit were, say 100, and the one half had to be reduced to 75 in order to establish equality, then clearly the relative intensities were as 4 : 3. In order to guard against the eye being confused by the intensities of the spectral regions on either side of the region dealt with, the eye-piece is provided with adjustable screens in order to shut off all the rays except those actually to be compared.

There are, however, several points of importance which must be attended to in order to make accurate measurements, and these necessitate the apparatus being more complex than the above simple description would foreshadow. In the first place, the original idea of Vierordt depends upon the assumption that the intensity of illumination is directly proportional to the width of the slit. This cannot be true with a slit of the ordinary type in which only one jaw is movable, so that the slit widens unsymmetrically. This difficulty was surmounted by Krüss who substituted for the Vierordt double slit one in which both jaws of each slit are equally moved in opposite directions by the micrometer screws. Each slit of the instrument is, there-

fore, opened or closed symmetrically. Again, the intensity of illumination is only proportional to the slit-width when the latter is small. If, therefore, the difference in intensity between the two spectra is very large, it is not possible to measure this only by altering the slit widths. The intensity of the brighter spectrum is first reduced by introducing a plate of neutral tinted glass, and the final adjustment made by altering the width of the slit. Several of these plates of tinted glass should be on hand, the absorption of which for the various spectral regions has been carefully determined.

In the second place it must be remembered that the loss of light suffered when a beam of light passes through an absorbing layer is not only that due to the absorption of the medium, but that a very appreciable amount is lost by reflection at the boundary surfaces. For example, if an absorption cell half full of the absorbing solution were placed in front of the slits of the Vierordt instrument so that the lower slit was illuminated by the light after passage through the absorbing layer while the upper slit received the light which passed through the upper and empty half of

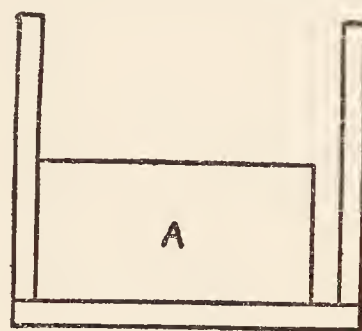


FIG. 15.

the cell, then the differences observed between the two spectra would not be that due to the absorption alone. The loss by reflection of the light would not be the same in the two cases, for, on the one hand, the reflection would be at a glass-solution surface, and in the other case it would be at a glass-air surface. As the indices of refraction for air and the solution are different the amount of loss by reflection would also differ. This difficulty may be removed by means of what is known as the Schultz corrector. This is a block of glass of the same quality as that of the walls of the cell and is shown at A in Fig. 15.

The internal thickness of the cell is made 11 mm., and that of the Schultz corrector 10 mm., and the depth of the latter is half that of the cell. The cell is filled with the absorbing solution and is set up in front of the slits of the instrument so that one slit receives the beam after passage through 1 mm. thickness of solution, and the other slit receives the beam after passage through 11 mm. If the cell and corrector are made of the whitest flint glass no appreciable absorption is introduced by the latter except in the extreme violet, whilst the difference in loss by reflection is reduced to a minimum.

The third point, and the most difficult of realisation, is the necessity that the two spectra should be in optical contact in the field of view. The eye is exceedingly sensitive to differences in intensity between two spectral images, provided that there is no sharply defined line of separation between them. It may be readily understood that however carefully the above cell be adjusted

in front of the Vierordt slits, it will practically be impossible to obtain the two spectra in contact without a dividing line. In order to bring the two spectra into contact H. and G. Krüss applied the so-called Hübner rhomb to the Vierordt instrument, the arrangement being shown in Fig. 16.

The two beams coming from the absorbing cell with the Schultz corrector enter the rhomb, and emerging thence they enter the slit and give two spectra in contact.

In the Vierordt instrument the intensity of the spectra is altered by varying the width of the slit, the assumption being made that the intensity is proportional to the slit-width, provided that this latter is kept small. Many forms of spectrophotometer have been devised from time to time, and a different method of altering the intensity adopted. In the Glan type the two beams are polarised at right angles to one another by suitable means, and they finally pass through a Nicol prism. A rotation of this will, therefore, decrease the intensity of one and increase the intensity of the other, and

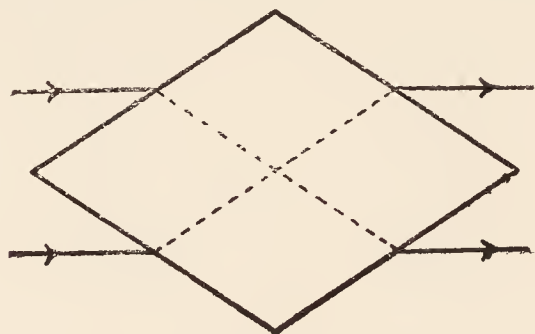


FIG. 16.

the relative intensities of the two may be calculated from the angle θ through which the Nicol is rotated, for $\frac{I}{I_0} = \tan^2 \theta$. In the Hübner instru-

ment only one beam is polarised, and the change in intensity is altered by the rotation of a Nicol prism as in the Glan instrument. In the older forms of the Hübner instrument the brighter beam, that is to say, that light which has passed through the thinner layer of absorbing solution, was polarised by reflection from two plane mirrors set at the polarising angle outside the slit. In the modern form the beam of light after transmission through the thinner absorbing layer is passed through a Nicol prism, and then the two beams are brought into optical contact by a special rhomb similar to that shown in Fig. 16, for the Vierordt instrument. The intensity is changed by a second Nicol, the angular rotation of which can be measured, and, if again θ be the angle of rotation necessary to bring about equality of the two spectra in the field of view, $\frac{I}{I_0} = \cos^2 \theta$.

The Hübner spectrophotometer has recently been much improved by Twyman, who has succeeded in reducing the experimental errors to a very small value. Twyman points out that the principal source of error lies in the fact that the rays of light in passing through the dispersing prism system are partially polarised. For this reason the beam which does not pass through the Nicol prism outside the slit will become partially polarised, and, therefore, will lose in intensity when the second or analysing

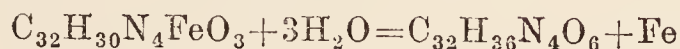
Nicol is rotated. As a matter of fact this error is corrected to a certain extent by the use of the Hübner rhomb owing to the fact that the principal planes of this rhomb and the dispersing prism are at right angles to one another. Twyman shows that by the use of a rhomb made of the same glass as the prism, and so cut that the angle of incidence on the face of the rhomb is the same as that on the prism face, the error is entirely eliminated, for the polarisation caused by the two, rhomb and dispersing prism, are then exactly equal and in planes at right angles, and thus the two exactly counterbalance one another.

Further, the instrument is made with a constant deviation prism so that the telescope and collimator are fixed and the spectrum caused to pass across the field of view by the rotation of the prism, the principle being the same as that of the spectrometer shown in Fig. 4. The accuracy obtained with this improved form of spectrophotometer is exceedingly great and far superior to that obtained with the ordinary form of instrument. In actual practice the instrument is adjusted as follows. The best source of illumination is a Nernst filament lamp, and the rays from this are directed into the instrument, and the analysing Nicol prism is set at the zero reading. Owing to the necessary loss of light caused in the one beam by the polarising Nicol the two beams will naturally appear of different intensities. In order to correct this error a wedge of neutral tinted glass is mounted outside the slit in the path of the brighter beam. This wedge is slowly moved until the two spectra appear exactly equal in intensity in the field of view. The instrument is then in adjustment, and in determining the extinction coefficient of a given solution, the solution is put in an absorption cell with a Schultz corrector, and this is properly mounted in front of the polarising Nicol and slit. When the analysing Nicol has been rotated so as to bring the two spectra again to equality, and as stated above, the angle of rotation is θ , the ratio of the intensities of the two beams I/I_0 will be given by $\cos^2 \theta$.

The instruments described in this section are naturally only applicable to work in the visible region. The experimental methods for quantitative investigation in the infra-red and the ultra-violet have already been discussed in Section VI.

IX. Qualitative and quantitative estimation of blood. Blood contains the highly complex iron-containing crystalline colouring matter called hæmoglobin. This hæmoglobin has the power of readily linking itself to an atom of oxygen, which is in such a labile state that it can readily be given up and oxidise the waste products of the tissues of the body. While living blood generally contains both the oxygenated and the deoxygenated hæmoglobin, the former is essentially a constituent of arterial, and the latter of venous, blood. This labile oxygen may, therefore, be considered as the respiratory oxygen of the animal system. Hoppe-Seyler has shown that hæmoglobin is decomposed by acids, and by alkalis in the absence of air into hæmochromogen (sometimes called reduced hæmatin), and finally into hæmatin. This process is apparently a hydro-

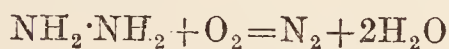
lysis, whereby an albumen, globin, is split off. If in this process hydrochloric acid be used, an intermediary product known as hæmin is formed, which is the hydrochloride of hæmatin (see BLOOD). Again, if hæmatin is heated with concentrated nitric acid or is dissolved in concentrated sulphuric acid, it dissolves, giving a solution of hæmatoporphyrin. This substance contains no iron, the iron atom having been withdrawn as a ferrous salt from the hæmatin. According to Nencki and Sieber the following equation expresses the preparation of hæmatoporphyrin from hæmatin—



Two reactions of hæmoglobin are of considerable importance, namely its oxidation and its reaction with carbon monoxide. When oxidised by a mild oxidising agent such as nitrites or potassium ferricyanide it is converted into a brown substance, methæmoglobin, the same substance being produced when hæmoglobin is exposed to air, as may be seen on the edges of wounds and on blood stains on cloth, &c.

The second reaction of hæmoglobin is the power which it possesses of absorbing carbon monoxide, a new compound being produced called carbon monoxide hæmoglobin. This is of great importance in dealing with cases of carbon monoxide poisoning.

The various derivatives of hæmoglobin may be prepared as follows: The blood is first defibrinated and diluted with 3 p.c. of caustic soda, when it is found to show the spectrum of oxyhæmoglobin. To reduce this back to hæmoglobin we may use freshly-prepared ammonium hydrogen sulphide, or better still, hydrazine hydrate, since in this case only nitrogen and water are formed



The addition of a few drops of concentrated potassium ferricyanide solution to diluted blood shows at once the spectrum of methæmoglobin.

If a drop of blood be warmed on a slide with one or two drops of glacial acetic acid and the mixture boiled over a small flame and then allowed to evaporate, the residue, when examined under the microscope, will show reddish-brown crystals of hæmin, known as Teichmann's crystals. Even an old blood stain gives the same, but better results are obtained in such a case if a small crystal of sodium chloride is added.

To prepare hæmin on a large scale, 1 volume of defibrinated and strained blood is added to 4 volumes of glacial acetic acid previously heated to 80°. As soon as the temperature has fallen to 55°–60°, the blood is again heated to 80°, and on cooling the crystals of hæmin separate out with characteristic silky lustre and dark-blue colour. These are allowed to settle for 12 hours, then decanted and washed with water, after which they are filtered off and washed with alcohol until the runnings are no longer coloured.

If the crystals are dissolved in very dilute caustic potash and then heated with dilute hydrochloric acid hæmatin is precipitated. This is then washed with water until free from chlorine.

Both hæmatin and hæmin dissolve in cold concentrated sulphuric acid to give hæmatoporphyrin, which is precipitated on the addition

of water. The absorption spectra of the different colouring matters are as follows:—

Oxyhæmoglobin shows two absorption bands in dilute solution which coalesce into one band when the solution is more concentrated.

Formánek 5880–5650 Å 5550–5260 Å

Naumann 5890–5680 Å 5570–5270 Å (maximum at 5500)

In stronger solution one band at 5940–5180 Å.

Hæmoglobin.—This only shows one band as a rule, though in very dilute solution a weaker band has been described as appearing on the red side.

Preyer 1871) . 5980–5400 Å (maximum at 5520)

Gamgee (1880) 5950–5380 Å (maximum at 5500)

Formánek . 5930–5700 Å and 5700–5400 Å

Carbon monoxide hæmoglobin.—Formánek describes two bands, 5810–5610 Å and 5500–5230 Å.

Methæmoglobin.—The neutral or faintly acid solution is chocolate-brown, whilst when made alkaline with ammonia it turns red. The former shows a well-marked band in the red, and two others which are very weak and may not be seen. The latter gives a principal band nearer to the blue and two faint bands. The fainter bands in both cases seem to agree with those of oxyhæmoglobin.

Neutral or faintly acid bands, Formánek, 6400–6250 Å, 5780–5680 Å, and 5540–5300 Å.

Alkaline, Ziemke and Müller, 6050–5890 Å, 5890–5790 Å, and 5580–5350 Å.

Hæmatin.—Alkaline solutions are red and acid solutions brown—

Alkaline solution (Naumann) . 6240–5750 Å

Acid solution shows a principal band in the red and a weaker one—

Naumann . 6600–6300 Å and 5890–5270 Å

Hæmatoporphyrin.—Acid alcoholic solutions are purple to bluish-violet. Alkaline solutions are red to red with a violet tinge—

Acid, 2 bands (Naumann), 6060–5910 Å and 5890–5440 Å

Alkaline, 4 bands (Formánek), 6330–6160 Å, 5890–5660 Å, 5200–5350 Å, and 5200–4980 Å.

For the quantitative estimation of blood the following values of the absorption ratios of oxyhæmoglobin, hæmoglobin, and carbonic oxide hæmoglobin may be given for the spectral regions specified (Hüfner):—

Substance	Limits of spectral region	Absorption ratio
Oxyhæmoglobin .	5650–5540 Å	0.002070
" .	5425–5315 Å	0.001312
Hæmoglobin .	5560–5540 Å	0.001354
" .	5425–5315 Å	0.001778
Carbonic oxide hæmoglobin	5650–5540 Å	0.001383
" " "	5425–5315 Å	0.001263

In the detection of blood stains, such as may occur in medico-legal cases, the stain is either washed out with water or digested with warm 10 p.c. sodium carbonate solution. The spectrum is noted and then the solution is treated with a reducing agent, for example, ammonium hydrogen sulphide or hydrazine hydrate, as described above, when the spectrum of hæmoglobin is formed. This is an exceedingly

delicate test; shaking with air restores the original spectrum, but a fresh addition of the reducing agent reproduces hæmoglobin.

Again, the hæmin and hæmoporphyrin test described above can be employed. In the detection of carbon monoxide poisoning the blood shows the spectrum of carbonic oxide hæmoglobin. This is somewhat similar to the oxy-hæmoglobin spectrum, but it is quite unaltered by ammonium hydrogen sulphide, and in this manner may be sharply differentiated.

X. Optical pyrometry. An important application of the spectroscope lies in the measurement of the intensity of the radiation from an incandescent source by direct comparison with that of a standard, for by this means the temperature of the former may be arrived at. Generally this comparison is carried out for red light, because, in the first place, the colour of the light emitted by a body varies very considerably with the temperature, and in the second place it allows the measurements to be made at lower temperatures. It must be remembered that the intensity of the radiation emitted by an incandescent substance is not only a function of the temperature, but also that it depends upon the surface and composition of the substance. In dealing with the radiation from any substance it is necessary, therefore, to set up a standard in terms of which all radiation laws can be expressed. This was first done by Kirchhoff, who defined the absolutely 'black body' as that which would absorb every radiation without reflection or transmission. He pointed out that the radiation of the 'black body' is purely a function of the temperature. Although no substance is known the surface radiation of which is exactly equal to that of the 'black body,' yet it is possible almost to realise the condition by maintaining a vessel at a constant temperature, and observing the radiation from the inside through a small hole in one of the walls. For high temperatures a porcelain tube may be electrically heated to a known temperature (determined by a thermocouple) and the radiation from the central portion examined. Such an apparatus is used in the calibration of optical pyrometers. It follows that in the optical measurement of temperatures the instrument will always give the 'black body' temperature corresponding to the intensity radiation dealt with. This temperature will, of course, only be the true temperature of the incandescent body when the latter is behaving as a 'black body.' Such a condition may frequently be realised, as, for example, in the determination of the temperature of a furnace by the examination of the radiation from the inside of a porcelain or metal tube projecting into the furnace. If, however, the 'black body' conditions are not obtained the optical pyrometer will usually give a temperature lower than the true value. In technical processes this error may not be of great importance, as, for example, when it is only necessary to reproduce certain given conditions with accuracy at any moment.

Before dealing with the methods of working with the various forms of optical pyrometers it is necessary to speak of the laws of radiation. The Stefan-Boltzmann law states that the total radiation emitted by the 'black body' is directly proportional to the fourth power of the

absolute temperature, and may be expressed as follows:—

$$I = k(T^4 - T_0^4)$$

where I is the total radiation from the black body at the absolute temperature T to the body at the absolute temperature T_0 , and k is a constant. It is well known that as the temperature of a body changes the wave-length of the maximum of the radiation varies, and Wien concluded that, if λ_m be the wave-length of the maximum energy, $\lambda_m T = \text{a constant}$. Combining this with the Stefan-Boltzmann law, Wien obtained the relation $I_{\max} T^{-5} = \text{constant}$, where I_{\max} is the energy corresponding to the wave-length λ_m and T is the absolute temperature of the 'black body.'

Even although these relations were deduced for the 'black body,' they hold good for other radiating surfaces, but, of course, the values of the constants are different. Wien's second equation is then modified to $I_{\max} T^{-a} = \text{constant}$.

Some further investigations of Wien led him to the following equation:—

$$I = b\lambda^{-5} e^{-\frac{c}{\lambda T}}$$

where I is the energy corresponding to the wave-length λ , e is the base of natural logarithms, T is the absolute temperature, and b and c are constants. Although it has been found that this expression does not hold good over long ranges of wave-lengths, yet it is sufficiently accurate for the ranges dealt with in optical pyrometry, and may be used for the calibration of these instruments. In practice the method of work with the optical pyrometer is as follows: Some standard of illumination is chosen, and the intensity of the red light of chosen wave-length emitted by the incandescent body is varied by some means until it becomes equal to that of the standard. For the calibration of this type of pyrometer Wien's third equation may be used—

$$I = b\lambda^{-5} e^{-\frac{c}{\lambda T}}$$

This may be written—

$$\log I = \log b - 5 \log \lambda - \frac{c}{\lambda T} \log e$$

$$\text{or} \quad \log I = C + \frac{K}{T}$$

where $C = \log b - 5 \log \lambda$, and $K = -\frac{c}{\lambda} \log e$.

Evidently, since we are dealing with the radiation of only one wave-length, there is a linear relation between $\log I$ and $1/T$. The instrument may be calibrated, therefore, from measurements of I at two known temperatures. A similar relation will hold good if the radiation be not that of the 'black body,' but the constants C and K will then be different.

In the Le Chatelier pyrometer the radiation from the incandescent source passes through an iris diaphragm, and is brought to a focus by a lens and examined through a screen of red glass with a Ramsden eye-piece. The rays from the standard of comparison pass down a tube at right angles to the first tube, and are reflected from a plane mirror into the eye-piece. The equality between the two radiations is produced by altering the aperture of the iris diaphragm.

If the radiation from the incandescent body is too great one or more plates of tinted glass are introduced, the coefficients of absorption of which are known, and the final adjustment done by the iris diaphragm. The effective aperture of this diaphragm can be obtained from the scale reading.

In the Wanner pyrometer the principle is the polarisation of both rays, as in the case of the Glan spectrophotometer described above. The radiations from the two sources are focussed on to two adjacent slits, and then after being rendered parallel by a collimating lens they pass through a direct-vision prism system. They then pass through a Rochon prism which resolves each beam into two portions polarised at right angles to each other. By means of a biprism and lens two red images oppositely polarised, one from each source, are focussed contiguous to each other on a third slit. The two beams then pass through a Nicol prism into the eyepiece. If the two intensities be equal, and the Nicol set at 45° with the plane of polarisation of each, both will appear of equal brightness. If, however, the two intensities be not equal, they may be equalised in the field of view of the eyepiece by rotating the Nicol. If the necessary angle of rotation of the Nicol is θ , the ratio between the intensities will be given by—

$$\frac{I_1}{I_2} = \tan^2 \theta$$

For the standard source of light in these instruments a Hefner standard amyl acetate lamp, a gasoline lamp, or an electric filament lamp fed with constant current may be used.

In the Féry instrument the total radiation from the incandescent object is measured. The rays are focussed upon a sensitive thermocouple, and the energy of radiation determined from the readings of a galvanometer connected with the thermocouple. In the calibration of this instrument the Stefan-Boltzmann law is employed.

V. PYROMETRY.

XI. Absorption spectra and their interpretation in reference to chemical constitution. The study of absorption spectra presents a very fascinating field of research, more especially in connection with the investigation of organic compounds, for the first question that arises is what the origin and meaning of the absorption bands may be. Since the existence of an absorption band means that the substance under examination has the power of selectively absorbing the light waves comprised within the band, it is a natural assumption to make that the substance possesses definite free periods of vibration and oscillates in those periods when stimulated by the light. According to this view the absorption spectra of a substance is a record of the vibration frequencies possessed by that substance. This is the commonly accepted explanation, and, indeed, Hartley, the pioneer investigator of the absorption spectra of organic compounds, called his absorption curves molecular vibration curves.

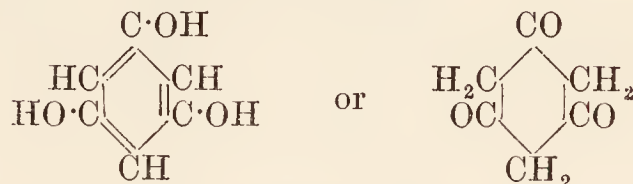
Acceptance of this explanation of absorption at once raises a second question, namely, what endows a molecule with its free periods of vibration. It is a very natural answer to reply that the determining factor must in some way be the constitution of the molecule, that is to say,

the nature and the arrangement of its component atoms. It is hardly possible to imagine that such a fundamentally characteristic property of a molecule can be independent of its atoms, and thus the conclusion is arrived at that the constitution of a molecule determines its absorption spectra. Although this conclusion seems to be secure, there is no obvious starting-point from which a definite theory can be built up. It is necessary for such a theory to possess definite data, specific cases, for example, of compounds of known constitution and their absorption spectra, in order to establish a connection between the two. Without such data it is impossible to make any progress.

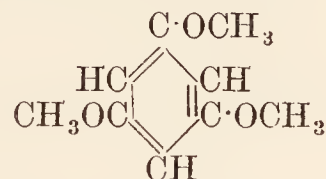
Now, Hartley investigated the absorption spectra of a very large number of organic compounds in the visible and near ultra-violet regions of the spectrum, having, in conjunction with Huntington, in 1879, been the first to discover that organic compounds exhibit absorption bands in the ultra-violet. It must be confessed that in spite of the great number of compounds examined no definite conclusions could be drawn. Hartley noted one or two facts, amongst which may be mentioned the following. According to him aliphatic compounds do not show selective absorption in the visible or ultra-violet regions, this property being restricted to aromatic compounds. He also proved that in general the substitution of a methyl group for a hydrogen atom makes little or no difference in the absorption spectrum. These were only general statements, and they still left the main problem unsolved.

About twenty years ago Hartley and Dobbie described some cases in which they were able to decide between two possible constitutions of a substance by comparison of its absorption spectrum with those of its two methyl derivatives, and the following examples may be quoted.

Phloroglucinol may be expressed by either of the two following formulæ:—

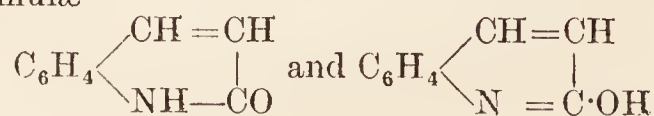


as far as the chemical evidence is concerned. Now, the constitution of the trimethyl ether of phloroglucinol is known to be—

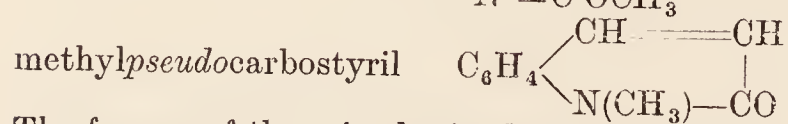
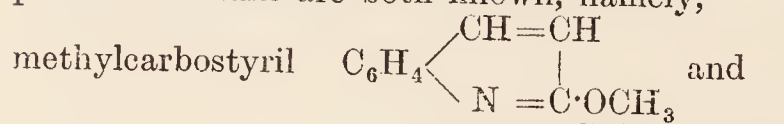


The absorption curves of phloroglucinol itself and the trimethyl ether are shown in Fig. 17, and it may be seen that they are almost exactly similar, and therefore there is no doubt that the two substances are of similar constitution, or, in other words, phloroglucinol must exist in the trihydroxy form.

A second case is the proof of the constitution of carbostyryl. Chemical evidence alone is not capable of differentiating between the two formulæ—



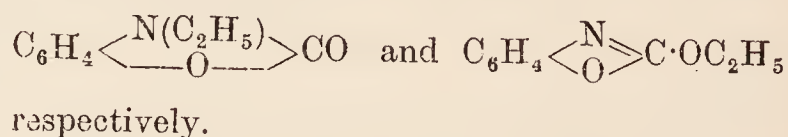
The methyl ethers corresponding to the above possible formulæ are both known, namely,



The former of these is obtained by the action of methyl iodide and sodium hydroxide upon

for the absorption curves show that its constitution is the same as that of the lactam ether.

The constitution of the lactam and lactim ethers is known to be



The absorption curves of the two ethers is shown in Fig. 19.

In a perfectly similar way isatin was proved to have the constitution represented by the formula—



During the next few years a number of workers entered this field, and it was not long before the specific theory was put forward that there exists a definite correlation between chemical constitution and absorption in the visible and ultra-violet. There is no doubt that such a theory possesses great fascination, and the results which were published seemed at first to offer considerable support and the theory was accepted by many.

Amongst the most interesting applications of this theory is that which deals with the well-known differences in absorption spectra exhibited by many substances when dissolved in different solvents. One of the most striking examples of this is shown by the group of nitrophenols, which give very different coloured

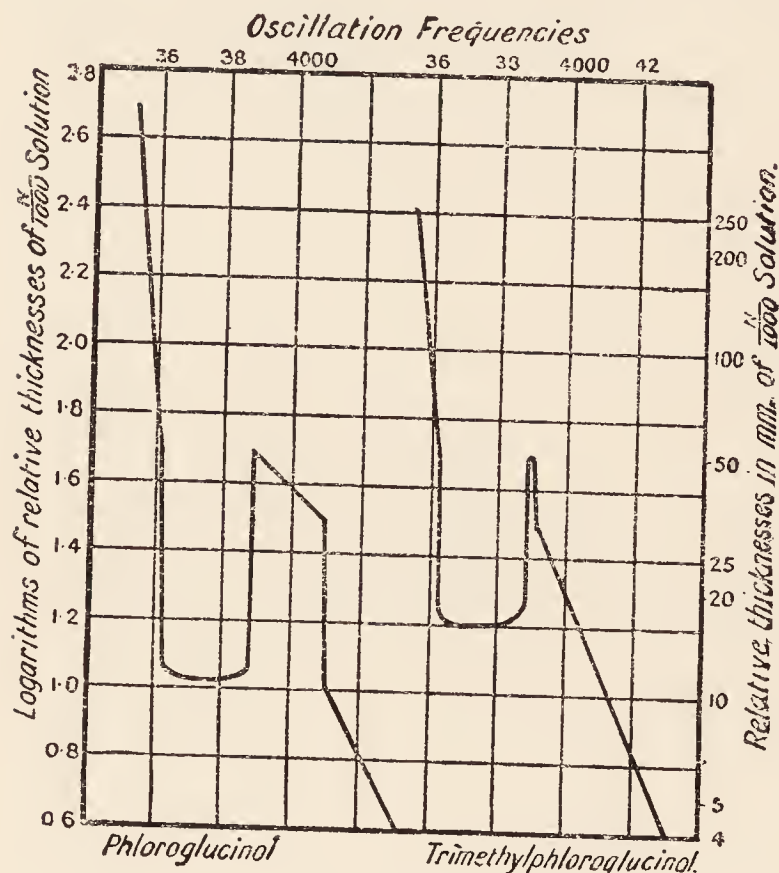
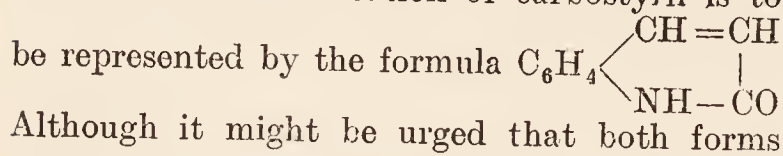


FIG. 17.

carbostyryl in methyl alcohol solution, whilst the latter is prepared by the action of methyl iodide upon the silver salt of carbostyryl.

The absorption spectra of the two ethers are shown in Fig. 18, and the absorption curve of carbostyryl is practically identical with that of methylpseudocarbostyryl. It therefore follows that the constitution of carbostyryl is to



Although it might be urged that both forms

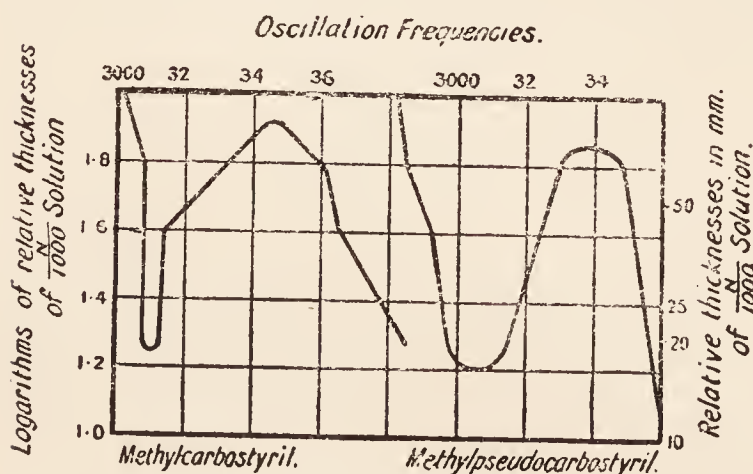


FIG. 18.

may be present in dynamic equilibrium, still, even if this were true, the amount of the ketonic form must be far in excess of the enolic form.

In exactly the same way the constitution of *o*-oxycarbanil was proved to be $\text{C}_6\text{H}_4 \begin{cases} \text{NH} \\ \text{O} \end{cases} \text{CO}$

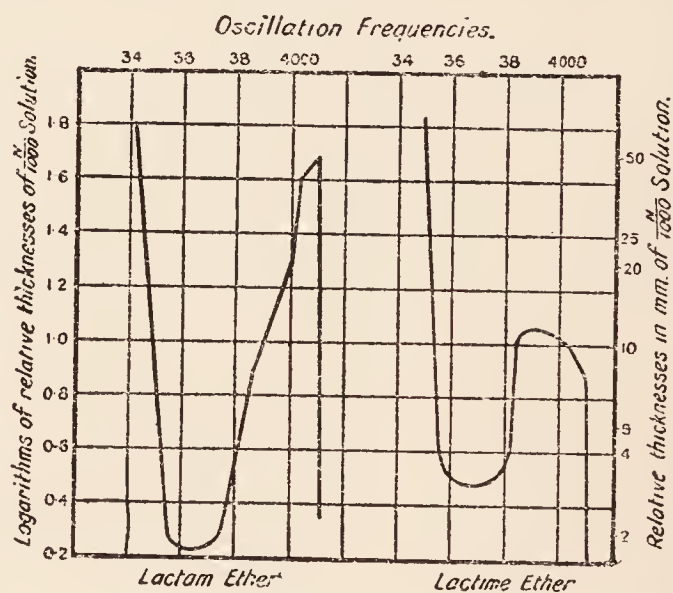
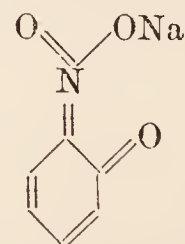


FIG. 19.

solutions in neutral and alkaline solvents. Thus *o*-nitrophenol gives a yellow solution in alcohol and a red solution in aqueous or alcoholic sodium hydroxide. Spectroscopic examination shows that the two solutions exhibit different absorption spectra, and therefore the nitrophenol, according to the theory, must possess a different constitution when in solution in the two solvents. This was readily explained by attributing a quinonoid structure to the alkali metal salt, e.g.



A similar explanation was applicable to all the nitrophenol and analogous compounds. When

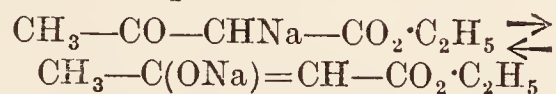
Hantzsch and Gorke succeeded in preparing very unstable and highly-coloured modifications of the nitrophenol ethers, to which they attributed a quinonoid structure, the argument seemed to be complete, and the structure-absorption correlation theory received great support. The very widespread application of the quinonoid theory to explain the colour of the dye-stuffs, supported as it was by the early work on absorption spectra, is one instance of the results achieved by this theory.

One of the greatest protagonists for this theory is Hantzsch, who has examined the absorption spectra of a great number of compounds, basing his interpretation of his results on the existence of a correlation between structure and absorption. Indeed, Hantzsch has taken up a rather more definite position than any other observer, in that he attributes a different structure to every absorption band shown by a given substance. One particular compound studied by Hantzsch and his co-workers is diphenylvioluric acid, which in the free state is only faintly yellow, whilst its alkali metal salts are differently coloured. The lithium salt is yellow, the sodium salt orange, the potassium salt red, the rubidium and caesium salts pure blue. The solutions of these salts show different absorption bands, and Hantzsch assumed that each band indicated the presence of a structurally different diphenylvioluric acid molecule.

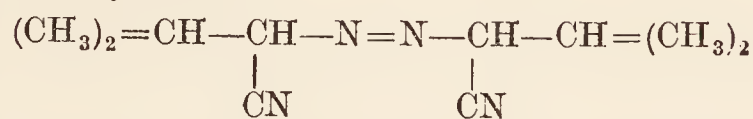
Although the structure-absorption correlation theory appeared to receive strong support from these and many other observations, no physical explanation of this correlation was found. It was a simple assumption to make that a change in absorption, that is to say, a change in vibration frequency, must be due to a change in structure, but no reason was found why any particular structure should give rise to an absorption band at all. No attention was paid to the fact, first observed by Hartley, that the majority of aliphatic compounds show no absorption bands in the visible or ultra-violet regions. This makes it all the more important to seek an explanation of the fact that the compounds dealt with by Hantzsch and by others exhibit any selective absorption at all in the visible or ultra-violet, quite independently of the changes they may show in change of solvent. This point has been entirely neglected by the upholders of the theory. Indeed, it may be said that the arguments adduced for each particular compound or group of compounds are purely *ad hoc*, no generalisation whatever being possible.

There is no doubt that as the knowledge of absorption spectra has become more extended the structure absorption theory as at first conceived has been found to be inadequate. Although there can be no question that some relationship must exist between the composition of a molecule and the frequencies of light which it absorbs, it has now become impossible to accept the theory that the relation is a direct one in the above sense, that is to say, there is no law which directly connects a given primary structure with a particular structure in the visible or ultra-violet region of the spectrum. Whereas it is perfectly possible that two different compounds may exhibit different absorption

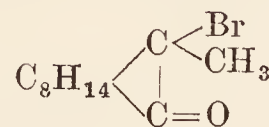
bands, the converse of this can by no means be accepted as true, for changes in the position of the absorption band exhibited in the visible or ultra-violet by a given substance cannot be taken as proof of change in the primary structure of that substance. A very typical instance of the danger of basing any conclusion as to structure is afforded by ethyl acetoacetate and its derivatives. As is well known, the parent ester is believed to exist in two forms: the ketonic form $\text{CH}_3\text{—CO—CH}_2\text{—CO}_2\cdot\text{C}_2\text{H}_5$, and the enolic form $\text{CH}_3\text{—C(OH)=CH—CO}_2\cdot\text{C}_2\text{H}_5$, and it was hoped that by a comparison of its absorption spectrum with those of the two ethyl derivatives $\text{CH}_3\text{—CO—C(C}_2\text{H}_5)_2\text{—CO}_2\cdot\text{C}_2\text{H}_5$ and $\text{CH}_3\text{—C(OC}_2\text{H}_5\text{)=CH—CO}_2\cdot\text{C}_2\text{H}_5$ the constitution of the free ester would be determined. It was found, however, that the parent ester exerts a greater absorptive power than either of the two ethyl derivatives, whilst the alkali metal salts exhibit a well-marked absorption band in the ultra-violet. On the structure-absorption correlation theory this showed that the ester cannot possess either the simple ketonic or enolic structure. A new suggestion was made, namely, that the absorption band was due to the tautomeric equilibrium



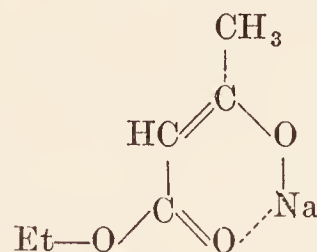
which obviously cannot be present in either of the two ethyl derivatives. Although this explanation seemed to be satisfactory, and although it was applied with apparent success to many other compounds, it was soon found to fail, since compounds in which no possible oscillation of double bonds occurs were found to exhibit well-marked absorption bands. Three instances of this are chloropicrin, CNO_2Cl_3 , azo-*iso*-butyronitrile



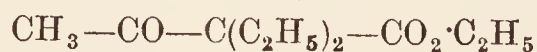
and the $\alpha\alpha'$ disubstituted derivatives of camphor, *e.g.*



Hantzsch suggested another explanation, namely, that the absorption band shown by the sodium salt of ethyl acetoacetate is due to the structure



the dotted line representing the play of secondary valencies between the sodium and oxygen atoms, a six-membered 'ring' being postulated. This explanation in its turn was negatived when it was found that ethyl diethylacetoacetate



also develops a strong absorption band, similarly to ethyl acetoacetate, when dissolved in alkali. It would indeed seem to be impossible to interpret any of the absorption bands shown by

these compounds in the ultra-violet on any simple structural theory.

As a matter of fact the structure-absorption theory fails on account of the exceedingly minute section of the spectrum to which it has been applied. The whole region of the spectrum, in which substances are known to exhibit absorption bands, extends from the wave-length 3000μ to the wave-length 0.1μ , whilst the visible and ultra-violet regions lie between 0.76μ and 0.22μ , which is less than $1/5000$ th part of the whole. Apart from any other question, it seems very arbitrary to base a fundamentally important conclusion on the observation of an absorption band in that small region, especially when it is remembered that that absorption band is only one of many shown by the substance throughout the whole spectrum.

The arguments against this theory, which are based on actual observations, are overwhelmingly strong, and the more important of these may be mentioned. In the first place, there are many substances which exhibit different absorption bands in the ultra-violet, according to whether they are examined in the liquid or gaseous state. This phenomenon is exhibited, for instance, by pyridine, piperidine, and benzaldehyde. The structural theory would demand a different structure for each of these compounds when existing in the two physical states. Some recent results afford strong evidence that the same is also true for ammonia, although the fact has not as yet been directly observed, since the absorption bands of liquid and gaseous ammonia lie in the very extreme ultra-violet between the wave-lengths of 0.2μ and 0.1μ . The difficulty of attributing two different structural formulæ to the molecules of pyridine and piperidine is sufficiently great, but in the case of ammonia such is impossible.

In the second place, there are the very remarkable changes in the absorption bands exhibited by a substance when in solution in different solvents. Instances of this phenomenon were mentioned above, namely, the changes shown by diphenylvioluric acid and by the nitrophenols. The difference in absorption shown by the latter in neutral and alkaline solvents can at first sight be explained by attributing the quinonoid structure to the alkali metal salts, and, indeed, this explanation appears to be supported by the discovery of the highly-coloured and unstable forms of the ethers by Hantzsch and Gorke. Since the corresponding nitroanilines exhibit the same absorption bands as the alkali salts these may also be given a quinonoid structure. Considerable difficulty, however, is then found with the nitrodimethylanilines, which exhibit the same absorption bands but are known not to be quinonoid. The difficulty is very materially increased when the nitrophenols and their ethers are examined in concentrated sulphuric acid solution. Although these solutions appear to the eye to be very similar in colour to the aqueous solutions of the alkali metal salts, they exhibit different absorption bands, which are two or more in number. The theory therefore demands the coexistence in concentrated sulphuric acid of two or more structures differing from those of the parent substances and their alkali metal salts—a maximum of five different structures for one nitrophenol. Many similar

instances might be given to illustrate the danger of formulating theories with insufficient evidence.

The strongest evidence of all is obtained from a study of the fluorescence exhibited by the phenols, their ethers, and certain analogous compounds. Anisole exhibits different absorption bands in alcoholic and concentrated sulphuric acid solutions, and therefore the theory demands that it must possess different structures in the two solvents. Now, in alcoholic solution anisole exhibits strong fluorescence, a fact that often escapes notice, since the fluorescence lies in the ultra-violet. The wave-length of this fluorescence is the same as that of the absorption band shown by anisole in sulphuric acid solution. This fact strikes right at the root of the structure-absorption correlation theory, the principal tenet of which is one structure one vibration frequency. The two vibration frequencies characteristic of anisole in two solvents are both now proved to be characteristic of anisole in alcoholic solution, one being exhibited as an absorption band and the other as fluorescence. Any argument therefore which attempts directly to connect one frequency with one structure must fall to the ground.

The theory of a direct connection between structure and absorption in the visible or ultra-violet is as a matter of fact far too crude, in that it attempts to explain vibration frequencies in a very restricted region of the spectrum by purely arbitrary structures, for which there is no positive evidence whatever. The theory offers no explanation of why a particular structure should be characterised by a particular vibration frequency. No explanation is offered of the fact that many substances of entirely different structure exhibit almost identical absorption spectra, nor of the fact that many compounds known to be similar in structure differ widely in their absorption spectra. This theory is still upheld by some, in spite of the overwhelming evidence against it, and in spite of the total absence of any physical explanation of a single observation, because the upholders work in water-tight compartments and ignore the absorption bands exhibited by their compounds in the spectral regions on either side of that which they have arbitrarily selected.

There are certain facts which have been observed in connection with absorption spectra and have been established beyond all question, and these cannot be ignored in the discussion of the problem. In the first place, it is definitely known that every substance possesses characteristic frequencies not only in the visible or ultra-violet, but also in the infra-red, these frequencies of course being exhibited as absorption bands. In discussing these frequencies it is convenient to divide the whole spectrum into four sections, the visible and ultra-violet from $\lambda=0.8\mu$ to 0.1μ , the short wave infra-red from $\lambda=20\mu$ to 0.8μ , the long wave infra-red from $\lambda=400\mu$ to 20μ , and the very long wave infra-red from $\lambda=3000\mu$ to 400μ .

The first real advance was made by Coblentz, who examined the absorption spectra of very many substances in the short wave infra-red and found that definite atomic groups exhibit characteristic absorption bands in that region, these bands being the same whatever the rest of

the molecule may happen to be. Coblentz's measurements are given in the following table:—

Compounds having the following groups	Show characteristic absorption bands at
CH_2 or CH_3	3.43, 6.86, 13.6, 13.8, and 14μ
NH_2	2.96, 6.1–6.15 μ
C_6H_6	3.25, 6.75, 8.68, 9.8, 11.8, 12.95 μ
NO_2	7.47, 9.08 (?) μ
OH	3.0 μ
NCS	4.78 μ
SO_4	4.55, 8.7, 9.1 μ

where $\mu = 0.001 \text{ mm.} = 10000 \text{ \AA.}$

This is the first observation which directly connotes constitution (not structure) with absorption.

A second phenomenon, which is one of great importance, is that the central frequency of every absorption band shown by a substance in the visible or ultra-violet is always an exact multiple of the central frequency of a very pronounced band shown by that substance in the infra-red. Reference has already been made to the fact that a given compound can exhibit different absorption bands in the visible or ultra-violet according to its physical state, the nature of solvent, &c., and it is these bands that form the basis of the structure of the structure-absorption theory. These bands, however, only differ in the fact that they are different integral multiples of the same infra-red band.

The study of the structure of absorption bands has also revealed some very important relationships. An absorption band, under high resolving power, is very frequently resolved into sub-groups, these in general being symmetrically distributed about a central sub-group. The central frequencies of all these sub-groups can be expressed as follows: $F \pm nS$, where F is the central frequency of the band, S is a constant, and $n=0, 1, 2, 3$, &c. It has been found that when such is the case the substance exhibits in the infra-red a series of bands with central frequencies nS . Furthermore, every compound possesses at least two of these subsidiary frequencies, S and T , exhibited both as series of bands in the infra-red, nS and nT , and also as sub-groups in the visible or ultra-violet bands shown by the compound. It is very important to note that these subsidiary frequencies are those recognised by Coblentz as being characteristic of definite atomic groups.

Then, again, these infra-red bands and their counterparts in the visible and ultra-violet bands can be resolved into lines which are grouped symmetrically round a central line, so that the frequencies of all the lines composing any band of the infra-red series nS or nT can be expressed by $nS \pm pA$, where again A is a constant and $p=0, 1, 2, 3$, &c. It has been also found that every compound exhibits at least two of these line series given by, say, $nS \pm pA$ and $nS \pm pB$.

There is yet another relationship which exists between all these frequencies exhibited by a compound. In the simplest case, such as that of water or sulphur dioxide, there are three very small characteristic frequencies, A, B, C , which lie in the very long wave infra-red, and there are two larger characteristic frequencies, S and T , in the long wave infra-red. Now the frequency S is the least common multiple of one pair of A, B , and C , whilst the frequency T is the least

common multiple of another pair. Lastly, the central frequencies of every absorption band shown in the visible or ultra-violet are exact multiples of the central frequency exhibited in the short wave infra-red, and this central frequency is either the least common multiple of all three frequencies A, B , and C , or a small multiple of that least common multiple.

Although it is known that the absorption bands exhibited by a compound in the visible and ultra-violet change according to the physical conditions, the absorption band in the short wave infra-red remains constant under all circumstances, and there is no doubt that this band is a fundamental characteristic of the molecule. Since it is known that the subsidiary frequencies S and T are characteristic of groups of atoms within the molecule, the conclusion follows that the still smaller frequencies A, B, C , in the very long wave infra-red are specifically characteristic of the atoms themselves. It has been found possible from this to formulate a theory which is based on the fundamental assumption that elementary atoms are characterised by definite quantities of energy or atomic quanta of energy. An atom can only absorb or radiate energy in terms of its atomic quantum, the frequency being established by the fact that the absorption or radiation of a quantum occupies a definite period of time. There is no need to develop this theory in detail, but it may be claimed that it affords a satisfactory explanation of all the arithmetical relationships described above. It also leads to the conclusion that a molecule is characterised by a quantum of energy, and hence must possess a characteristic and fundamental frequency of its own which lies in the infra-red, and, further, that it must exist in one of a number of possible phases. These phases differ in their energy content, any two consecutive phases differing by one molecular quantum of energy. Each molecular phase when examined spectroscopically exhibits its fundamental molecular frequency and also a characteristic phase frequency of its own, which is an exact multiple of the molecular frequency, the phase frequency always being in the visible or ultra-violet. Lastly, each phase is characterised by its own specific chemical reactivity.

These deductions from the molecular phase hypothesis are capable of giving a quantitative explanation of all absorption spectra observations and of the phenomena of chemical reaction and reactivity. A few instances of its application to visible and ultra-violet absorption may be given. The phase in which a molecule exists depends on the conditions in which it finds itself, and by altering these conditions it is possible to change that phase. Since the essential characteristic of each phase is its energy content it is possible to alter the phase by supplying energy to the molecule or allowing energy to be radiated by the molecule, the amount of energy for a single phase change being one molecular quantum. There are three methods of supplying energy to a molecule, namely, by exposing it to infra-red radiation, by exposing it to short wave radiation, and by the action of a material catalyst. The first method, which is merely a question of heating, can readily be understood, since the molecule absorbs the necessary increment of energy at its characteristic infra-red

frequencies. The second method is equally straightforward, since the energy is absorbed at the frequency in the visible or ultra-violet characteristic of the initial phase of the molecule. It is important to note that in this case the quantum of energy absorbed is far greater than is required for the phase change, and that the balance is radiated as fluorescence. This phenomenon will be discussed in greater detail below. The third method, namely, the action of a material catalyst, may require some explanation. The formation of a loose addition complex between two molecules is a well-recognised phenomenon, but the conditions governing the stability of such a complex are not dealt with in the literature. The molecular phase hypothesis establishes the fact that there are two ways in which such a complex can be formed and stabilised, both of these being completely supported by experimental evidence. In the first place, both components in associating together may jointly lose energy, thereby passing into phases of lower energy content. This type of complex formation is accompanied by evolution of heat, and may be exemplified by the combination of aniline with hydrogen chloride to form the hydrochloride. The change in phase of the aniline molecules can readily be recognised by absorption spectra methods, since in forming the salt the absorption band of aniline shifts very materially towards the shorter wave-lengths. The corresponding phase change of the acid molecules has not as yet been observed, because the absorption bands of the initial and final phases lie in the very extreme ultra-violet beyond the limit of a quartz spectrograph working in air.

In the second place, a molecule of one compound can give up one or more quanta of energy to a molecule of the other component, no energy being lost to the surroundings. The complex is thereby stabilised, since it cannot dissociate unless the energy is restored back again. It is obvious that the molecule which receives the energy is converted into a phase of higher energy content, the resultant phase depending on the number of quanta which the molecule has received. This is the common occurrence when a substance is dissolved in a solvent, and hence the phase change and the accompanying change in the absorption band in the visible or ultra-violet can at once be understood, without any need of postulating a change in primary structure to account for the phenomenon. A single molecule may be changed into many different phases, each with its own absorption band by the use of as many different solvents. A very typical instance of this is the compound already mentioned, viz. diphenylvioluric acid, which exists in different phases when associated with LiOH, NaOH, KOH, and RbOH. Similar instances are afforded by the nitrophenols which exist in different phases in solutions in alcohol, NaOH, and concentrated sulphuric acid.

At this stage reference may be made to the fact that when large numbers of molecules are considered it by no means follows that they must all exist in one phase and one phase only. In general, when a substance is examined, it is found to exist as an equilibrium mixture of two or more molecular phases. Few substances

exist in one phase, at any rate those the absorption bands of which lie in the visible or near ultra-violet. The nearest approach to existence in one phase only is exhibited by the dye-stuffs, the intensity of colour of these being due to this fact.

The more common phenomenon of the co-existence in equilibrium of two or more phases is of some importance at this juncture in case any misapprehension arises. The absorption band exhibited by many substances in solution is the same as that exhibited by the pure homogeneous substance. It will always be found, however, that the molecular absorptive power is greater in solution, owing to the fact that the solvent has not established a new phase, but has shifted the equilibrium in favour of the phase with higher energy content, i.e. the phase with the absorption band of smaller frequency.

As has already been explained, every substance must exhibit at least one absorption band in the visible or ultra-violet region, and in many cases this band lies in the extreme ultra-violet beyond the ordinary limit of $\lambda = 210\mu\mu$, which is set by the photography of the spectrum with a quartz spectrograph working in air. Such substances used to be recorded as being diactinic, but it is now known that every one exhibits an absorption band in the very extreme ultra-violet, and, further, it has also been proved that with rare exceptions all substances, even though they exhibit an absorption band in the visible or near ultra-violet, exist in the main in a phase with its frequency situated in the extreme ultra-violet. The existence of these absorption bands of very small wave-lengths has been established by measurements of refractivity.

An important deduction from the molecular phase hypothesis is the metastable existence of a compound in a phase of higher energy content than the normal characteristic of that compound. A familiar instance of this is afforded by trinitrotoluene, which normally exhibits an absorption band on the borderline between the visible and ultra-violet and thus is cream-coloured. On solution in a basic solvent such as piperidine trinitrotoluene is partly converted into a phase of higher energy content with its absorption band in the blue, and therefore exhibits a red colour. If the piperidine solution is poured into excess of hydrochloric acid the trinitrotoluene is precipitated, and from this the red-coloured phase may be obtained by extraction with benzene as a red oil insoluble in that solvent. This red phase is metastable and readily reverts to the normal cream-coloured phase. Another instance of the same phenomenon is found in the so-called *aci*-nitrophenol ethers of Hantzsch and Gorke, which simply consist of the ether in a phase of abnormally high energy content. These coloured substances were at one time believed to have the quinonoid structure, but there was no evidence adduced in support of that view. Many examples are known of compounds which exist in two modifications of different degrees of stability. These are all readily to be explained by difference of molecular phase.

Mention was made above of the phenomena of fluorescence and phosphorescence, and since these are intimately associated with absorption they may be briefly discussed. When a molecule absorbs energy at the frequency characteristic

of the phase in which it exists, it is in general converted into a phase of higher energy content. The energy absorbed, however, is always far greater than is necessary for the phase change, and the balance is radiated again to the surroundings. This radiation takes place in one of two ways. It may either be evolved at the infra-red frequencies characteristic of the molecule or at the frequency characteristic of the newly-produced phase. When the second alternative occurs the phenomenon is known as fluorescence, and it will at once be understood how this explains the observations referred to above in connection with the ethers of the phenols. In alcoholic solution these compounds absorb energy at one frequency and radiate it at another and smaller frequency. In the sulphuric acid solution these compounds absorb the second and smaller frequency. The phenolic compound in alcoholic solution exists in a phase I, and in absorbing energy at the frequency characteristic of that phase is converted into a new phase II, and the balance of energy, being exactly equal to that characteristic of phase II, is radiated at the frequency appertaining to that phase. In the sulphuric acid solution the compound exists in phase II, and therefore absorbs the same frequency as is emitted by the alcoholic solution in the form of fluorescence.

Phosphorescence is a very analogous phenomenon, the essential difference being that the energy instead of being instantaneously radiated is retained for a long or short period by the system existing in a metastable condition.

Many other instances might be given of the application of the molecular phase hypothesis to absorption spectra, but perhaps they are too obvious to need mention. Although the cases quoted have been discussed in a qualitative way, the theory rests on a completely quantitative basis. Sufficient has been said to show that the theory must be capable of explaining other physical phenomena, such as latent and specific heats, &c., and it may be stated that these have found satisfactory quantitative expression in terms of phases. The three physical states, gas, liquid, and solid, are determined by a different phase equilibrium. Similarly the phenomenon of allotropy is also one of phase equilibria. Such questions, however, lie outside the purview of absorption spectra, and are only mentioned in order to justify the statement that the phase hypothesis rests on a secure quantitative basis.

The question might well be asked as to how any question of chemical constitution could be decided by absorption spectra observations, since there is no relation between structure and absorption in the visible and ultra-violet. The method can be used, as indeed Hartley and others used it, with complete confidence, provided that no change in phase breaks the thread of the argument. It is a well-recognised fact that an acid and its ethyl ester normally exist in the same phases, and hence if the constitution of one is definitely known, and the two exhibit the same absorption, the conclusion may safely be drawn that the two have analogous formulæ. The method entirely and obviously breaks down when a change of phase supervenes. When a base is converted into its salt a change of phase frequently takes place as in the case of aniline and

aniline hydrochloride, where the primary structure of the aniline molecule is the same in each.

In fine the phase hypothesis does not preclude the use of absorption spectra in deciding certain problems of constitution, but it shows that great care must be used in interpreting the results. It has been established beyond all question that one and the same molecule with fixed primary structure can exhibit different absorption bands under different conditions, and from this it follows that a change in absorption must on no account be accepted as proof of a change in primary structure. A change in primary structure means the rearrangement of the component atoms of a molecule with the formation of new atomic groups. Such change may or may not cause a change in the absorption band in the visible or ultra-violet, for the phases of the two compounds may be similar or different. The effect of a change in the primary structure is to be looked for in the subsidiary frequencies which, as has been explained, are established by the atomic groups. These subsidiary frequencies can often be found from the sub-groups of the absorption band in the visible or ultra-violet. If, however, the band does not exhibit any sub-groups, then the subsidiary frequencies must be found from measurements of the absorption in the infra-red.

One instance of the reality of these subsidiary or intramolecular frequencies may be quoted, namely, that of naphthalene, one of the ultra-violet bands of which shows a series of sub-groups with a constant wave-number difference of $1/\lambda = 47.12$. This number must be characteristic of an atomic group present in the molecule of naphthalene. The two main atomic groups are the phenyl group and the olefinic group— $\text{CH}=\text{CH}-\text{CH}=\text{CH}-$ and, therefore, either benzene or an olefine should exhibit infra-red bands with central wave-lengths of 21.22μ , 10.61μ , 7.07μ , 5.30μ , 4.24μ , &c., i.e. the reciprocal of $47.12 \times 1, 2, 3$, &c. Benzene shows no such bands, but in the case of ethylene (all the olefines being very similar) Coblentz finds absorption bands with centres at 10.8μ , 6.98μ , 5.30μ , and 4.32μ , his measurements not extending beyond the wave-length of 15μ . As long as the subsidiary frequency is exhibited by naphthalene the primary structure must be unchanged, whatever changes may be observed in the ultra-violet absorption band.

Finally, the question may be asked as to how the chemist is to represent by means of formulæ the change that is associated with a change of phase, but not of primary structure. The change is one of a finer order than structural change, and too little is as yet known of its nature to represent it by formulæ. It is bound up in some way with residual affinity and secondary valency, but though the phenomena have long been recognised, and though attempts have been made to give them quantitative expression, such attempts have met with little success. Although the phase hypothesis seems capable of affording such quantitative expression, yet up to the present little advance has been made in this direction.

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E. C. C. B.

SPECULAR IRON ORE *v.* IRON; also **HÆMATITE**.

SPECULUM METAL. An alloy of 1 molecular proportion of tin and 4 of copper and a small quantity of arsenic, used for making the mirrors of reflecting telescopes.

SPEISS *v.* COBALT.

SPELTER *v.* ZINC.

SPENCERITE. Hydrated basic zinc phosphate $\text{Zn}_3(\text{PO}_4)_2 \cdot \text{Zn}(\text{OH})_2 \cdot 3\text{H}_2\text{O}$, crystallised in the monoclinic system. It forms scaly aggregates with a snow-white colour and brilliant pearly lustre on the perfect cleavages. Crystals are small and rare, and usually show lamellar twinning. Sp.gr. 3.144, $H.=3$; readily soluble in acids. Three-fourths of the water is lost at 160° , whilst the remainder is expelled between 200° and 400° . The calcined mineral is yellow when hot, indicating the presence of a basic salt of zinc. It occurs in some abundance forming large stalactites, thinly encrusted with hemimorphite, in a cave in the H.B. zinc-lead mine near Salmo in British Columbia. About a hundred tons of ore, consisting mainly of spencerite (Zn 48.5 p.c.), were taken from this cave (T. L. Walker, Univ. Studies, Geol. Ser. No. 10, Toronto, 1918).

The same name has also been applied (C. Hlawatsch, 1903) to an artificial furnace product consisting of the orthorhombic modification of iron carbide Fe_3C or $(\text{Fe}, \text{Mn})_3(\text{C}, \text{Si})$, corresponding with Spiegeleisen; as distinct from the triclinic modification, corresponding with ferro-manganese.

L. J. S.

SPERM OIL *v.* OILS, FIXED, AND FATS.

SPERMACETI *v.* WAXES.

SPERMACETI, VEGETABLE, *Insect wax v.* WAXES.

SPERMIN *v.* SYNTHETIC DRUGS.

SPERRYLITE. A mineral of interest as being the only naturally-occurring compound of platinum. It is the diarsenide PtAs_2 , and forms minute, tin-white crystals, which are cubic with the same degree of symmetry as iron-pyrites (FeS_2). It was found in 1889 as a loose crystalline powder, filling small pockets in decomposed

pyritic ore at the Vermillion gold mine in the Algoma district (22 miles west of Sudbury), Ontario. Minute crystals are also obtained by dissolving in acid the copper-pyrites from this mine and other neighbouring mines. The platinum detected in small amounts (0.006–0.24 p.c.) in the pentlandite and nickeliferous pyrrhotite of Sudbury, Ontario, is perhaps present as sperrylite. A few minute crystals of sperrylite have been isolated from the platiniferous copper ore (covellite) of the Rambler mine in Medicine Bow Mtns., Wyoming. Other localities are in North Carolina, British Columbia, and Siberia, but the mineral is always of very sparing occurrence. The frequent presence of traces of platinum in sulphide ores of nickel and copper is, however, a promising indication for future discoveries (*v. F. W. Clarke, Data of Geochemistry, Bull. U.S. Geol. Survey, No. 330, 1908, 610.*)

L. J. S.

SPESSARTITE *v. GARNET.***SPHACELINIC ACID** *v. ERGOT OF RYE.***SPHÆROSIDERITE** *v. CHALYBITE.***SPHALERITE** *v. ZINC-BLENDE.*

SPHENE, or Titanite. Calcium titanosilicate CaTiSiO_5 , crystallised in the monoclinic system, often in wedge-shaped forms, hence the name, from $\sigma\phi\eta\nu$, wedge. Iron and sometimes yttrium and cerium earths are present in small amount. Crystals range from pale greenish-yellow and transparent to black and opaque. Sp.gr. 3.4–3.6. The mineral is remarkable for its high dispersion; the refractive index γ being 1.9841 and 2.0601 for wavelengths $718\mu\mu$ (red) and $460\mu\mu$ (blue) respectively, difference 0.0760. The peculiar interference-figure shown in convergent polarised light is due to the wide difference in the optic axial angle for different colours. Sphene is of wide distribution as an accessory constituent of many kinds of igneous rocks. Large crystals are found in the apatite veins in the south of Norway, and in crystalline limestone with apatite in Renfrew Co., Ontario. Transparent crystals of a good colour are found with adularia, quartz, and asbestos in crevices of the gneissic rocks of the Alps. These are occasionally used as gem-stones, but owing to their comparatively low degree of hardness ($H.=5\frac{1}{2}$) they soon show signs of wear. The faceted stones show brilliant flashes of prismatic colours; the high dispersion exceeding that of diamond. Crystals of sphene, and also of the corresponding stannosilicate (CaSnSiO_5), have been obtained artificially.

L. J. S.

SPIEGEL-EISEN *v. IRON.*

SPIKENARD OIL (*Valeriana celtica* [Linn.]) is a thick yellow oil with an odour resembling that of valerian and hazelwort oils. It has sp.gr. 0.9693 at 20°; $[\alpha]_D -42^\circ$; saponification value 62.5; ester value (after saponification and acetylation) 71.9. It contains palmitic acid and a sesquiterpene, b.p. 255°, sp.gr. 0.9359 at 20°, $[\alpha]_D -30.88^\circ$ (J. Soc. Chem. Ind. 1909, 1272).

SPILANTHOL. The pungent principle of Para cress (*Spilanthus oleracea*) $\text{C}_{37}\text{H}_{64}\text{O}_3\text{N}_2$, first isolated by Gerber (Arch. Pharm. 1903, 241, 270), a reddish-yellow oil which when heated with alcoholic hydrochloric acid gave a base isobutylamine $\text{C}_4\text{H}_{11}\text{N}$, and an acid $\text{C}_{14}\text{H}_{28}\text{O}_2$ (see also Yasuhiko Asahina and

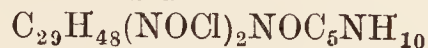
Michizo Asano, J. Pharm. Soc. Japan, 1920, No. 460, 503).

SPINACANE. A hydrocarbon $\text{C}_{29}\text{H}_{60}$ prepared by Chaston Chapman (Chem. Soc. Trans. 1923, 123, 770) by the hydrogenation of spinacene (*q.v.*). Not a normal but probably an isoparaffin.

A. C. C.

SPINACENE $\text{C}_{29}\text{H}_{48}$, a liquid hydrocarbon found by Chaston Chapman in the liver oils from certain fishes of the natural family of the *Spinacidæ*. B.p. 260° corr./9 mm.; $D_{20}^{20} 0.8588$; $n_D^{20} 1.4951$; refractive index at 20° for D line 1.4956; specific refraction 0.3396; molecular refraction 134.5. Thin layers of the hydrocarbon, when exposed to the air, form a hard film, owing to the absorption of oxygen, similar to that given by linseed oil.

Hexahydrochloride $\text{C}_{29}\text{H}_{48}6\text{HCl}$, solid, crystallising in plates and needles, m.p. 126. At about 140°–150° freely evolves hydrogen chloride. *Hexahydrobromide* $\text{C}_{29}\text{H}_{48}6\text{HBr}$, white crystals, m.p. 132° (decomp.). Insoluble in alcohol or ether. Sparingly soluble in acetic acid, carbon tetrachloride or chloroform; moderately soluble in pyridine or trichloroethylene. *Trinitrosochloride* $\text{C}_{29}\text{H}_{48}(\text{NOCl})_3$, pale, buff-coloured substance, moderately stable when dry. *Dinitrosochloride mononitrolpiperidide*



a buff-coloured solid, readily soluble in dilute acids and in the ordinary organic solvents. M.p. 146° (decomp.). Forms a crystalline hydrochloride. *Trinitrolpiperidide*



pale brown substance, readily soluble in alcohol. *Dinitrosochloride mononitrolbenzylamide*



buff coloured powder. *Trinitrolbenzylamide*



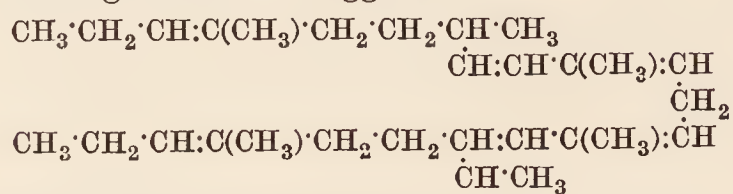
pale yellow powder, readily soluble in dilute acids. *Hexanitrosochloride* $\text{C}_{29}\text{H}_{48}(\text{NOCl})_6$. *Nitrosate* $\text{C}_{29}\text{H}_{48}(\text{NO}\cdot\text{NO}_3)_3$, yellow unstable substance, gradually forming a dark brown spongy mass. By hydrogenation spinacene is converted into spinacane $\text{C}_{29}\text{H}_{60}$, a colourless, odourless oil, $D_{20}^{20}=0.8119$; b.p. 280°–281° corr./24 mm.; refractive index at 20° for D line 1.4532; specific refraction 0.3330; molecular refraction 135.8.

Dry distillation in presence of sodium results in a small yield of a cyclic hydrocarbon $\text{C}_{10}\text{H}_{18}$, $D_{20}^{20}=0.8125$; b.p. 170°–175°; refractive index for D line at 20° 1.4565; specific refraction 0.3353; molecular refraction 46.3, and is probably a methyl-propylidene-cyclohexane.

Decomposition by means of an incandescent platinum wire in the vapour of the hydrocarbon results in a large yield of an olefinic hydrocarbon, *heparene* $\text{C}_{10}\text{H}_{18}$, $D_{20}^{20}=0.8008$; b.p. 79–83/33 mm.; refractive index for D line at 20° 1.4584; specific refraction 0.341; and the molecular refraction 47.1. Forms a tetrabromide, white crystals, m.p. 136° (corr.).

On oxidation with hydrogen peroxide in acetic anhydride solution, spinacene yields a peroxide $\text{C}_{27}\text{H}_{48}\text{O}_8$, further oxidation of which

by $K_2Mn_2O_8$ gives an acid $C_{25}H_{44}O_7$. The following formula is suggested:—



(Chem. Soc. Trans. 1917, 111, 56; *ibid.* 1918, 113, 458; *ibid.* 1923, 123, 770).

Tsujimoto (J. Ind. Eng. Chem. 1917, 9, 1098) had independently detected the presence of an unsaturated hydrocarbon, *squalene*, in the liver oil of the basking shark (*Cetorhinus maximus*). This hydrocarbon forms hexahydro-halides which may be readily crystallised and serve for the identification of the hydrocarbon. It has $n_D^{20} = 1.4965$, and is readily soluble in ether, petroleum spirit, carbon tetrachloride and acetone, and sparingly soluble in cold alcohol and glacial acetic acid. When mixed with 1 p.c. of cobalt resinate it dried in about 10 days in winter to a colourless smooth film. The product obtained by complete hydrogenation of squalene is an oil which sets to a transparent jelly at -80° , and becomes mobile again at -35° . According to Tsujimoto (J. Ind. Eng. Chem. 1920, 12, 63), squalene has the composition $C_{30}H_{50}$, and is possibly identical with Chapman's spinacene. It occurs most frequently in the liver oils from sharks belonging to the family *Squalidae*, but is also present in notable quantity in the liver oils of *Scylliorhinidae*, *Chlamydoselachidae* (frill-shark), *Dalatiidae*, and *Cetorhinidae* (basking-shark). It is also present in the oil from shark's eggs.

A. C. C.

SPINACH, *Spinacia oleracea* (Linn.). Several varieties are known. The leaves are used as a vegetable.

Average composition (König)—

Other							
Water	Protein	Fat	Sugar	N-free extract	Fibre	Ash	
89.2	2.7	0.5	0.1	3.5	0.9	2.0	

About half the total nitrogen exists as real proteid, and the N-free extract includes about 0.9 p.c. of pentosans.

Spinach is remarkable for the high proportion of iron which it contains, largely in the form of organic compounds. Cf. Lichtui, Amer. J. Pharm. 1924, 96, 361; Analyst, 1924, 49, 390.

König gives, as the composition of the ash—

K_2O	Na_2O	CaO	MgO	Fe_2O_3	P_2O_5	SO_3	SiO_2	Cl
16.6	35.3	11.9	6.4	3.4	10.2	6.9	4.5	6.3

Serger (Chem. Zentr. 1906, i. 1668) found that winter spinach contained from 86 to 89.5 p.c. of water, 9.5 to 13.3 p.c. of combustible matter, and 1.9 to 3.1 p.c. of ash. 100 grms. of the dry substance contained, on the average, 0.140 gm. of iron. From 100 grms. of fresh winter spinach, dilute alcohol extracted 4.3 grms. of substance which contained 0.179 p.c. of iron and gave 26.23 p.c. of ash, while the residual material yielded 8.7 grms. of dry substance containing 0.066 p.c. of iron, and gave 9.18 p.c. of ash. A considerable amount of the iron was also present in the matter extracted by a mixture of benzene, chloroform, and ether from the fresh leaves.

The amount of iron in spinach may be considerably increased by the addition of ferric

oxide to the soil (Czadek, Chem. Zentr. 1904, i. 832).

For the great increase of crop resulting from the use of sodium nitrate and other artificial manures, v. Dyer and Shrivell, J. Roy. Hort. Soc. 1903, 27, part 4).

Microscopic examination of a sample of preserved spinach suspected of adulteration with foreign leaves revealed the epidermis and parenchyma of the spinach leaf, round pollen grains, the rounded anthers (from 0.2 to 0.5 mm. in diameter and having a mammillary surface), and vestiges of the staminal threads. Only the male flowers were found, the absence of female flowers being probably explained by the practice, among the seed-growers, of uprooting the male plants after fertilisation. Such plants are doubtless bought at a cheap price, and preserved, and, although not adulterated, are of inferior quality, especially if more or less fibrous parts of the petioles should remain in the product. Proper plant should, however, remove such fibrous material (L. Gobert, Ann. Falsificat. 1924, 17, 158; Analyst, 1924, 49, 342).

H. I.

SPINEL (*Spinelle*, Fr.). A double oxide of magnesium and aluminium or a magnesium aluminate, $MgO \cdot Al_2O_3$ or $MgAl_2O_4$, crystallised in the cubic system. The name is also applied to a large isomorphous group of cubic minerals with the general formula $R''R'''O_4$, where $R'' = Mg, Fe, Zn, Mn$, and $R''' = Al, Fe, Cr, Mn$. Other members of this group are magnetite, chromite, franklinite, gahnite (*qq.v.*). *Picotite* is a chrome-spinel, $(Mg, Fe)O \cdot (Al, Cr)_2O_3$, intermediate between spinel proper and chromite. Spinel proper is of importance as a gem-stone. When red it is known as 'ruby-spinel,' 'spinel-ruby,' or 'balas-ruby,' and is often mistaken for the true ruby or corundum (*q.v.*), from which it is distinguished by its optically isotropic character, lack of pleochroism, and lower sp.gr. (3.6–3.7) and hardness ($H. = 8$). Large numbers of small, water-worn crystals are found in the gem-gravels of Ceylon. These are octahedral in form and often twinned on a face of the octahedron (hence the term spinel-twin for this type of twinning). Blue spinel ('sapphire-spinel') is much less common; stones of excellent quality have been made artificially (*v. GEMS, ARTIFICIAL*). Spinel is much used for the jewelled pivot-supports of clocks and watches.

L. J. S.

In the cases of crystals of the formulæ $ZnAl_2O_4$, $ZnCr_2O_4$, $ZnFe_2O_4$, $MgAl_2O_4$, $MgCr_2O_4$, $MnAl_2O_4$, $MnCr_2O_4$, $CdCr_2O_4$, and $FeFe_2O_4$, the distances between adjacent atomic centres have been calculated from the densities, and the positions of the oxygen centres determined. The densities of the compounds $MgFe_2O_4$ and $MnFe_2O_4$ are calculated to be 4.47 and 4.90 gr./cm.³, respectively. When the oxygen radius (the distance from the atomic centre to the valency electron-pair) is assumed to be 0.65 Å, atomic radii may be computed as follows: Zn^{+2} , 1.31 Å; Fe^{+2} , 1.27–1.30; Mg^{+2} , 1.29; Mn^{+2} , 1.39; Cd^{+2} , 1.51; Fe^{+3} , 1.38; Al^{+3} , 1.26; Cr^{+3} , 1.35. It is considered that the empirical formula $R''R'''O_4$ is the only one which correctly represents the structure of the spinels in the crystalline state. A partial explanation of the

cause of ferromagnetism may possibly be found in the suggestion that it arises from a concentration of electron triplets in the same end of each atomic kernel (Maurice L. Huggins, *Physical Rev.* 1923, 21, 509-516; *J. Chem. Soc.* 1923, 124, ii. 646-647).

SPIRARSYL. Trade name for sodium arsenophenylglycinate. See ARSENICALS, ORGANIC.

SPIRIT OF AMMONIA *v.* AMMONIA.

SPIRIT OF HARTSHORN *v.* AMMONIA.

SPIRIT OF SALT *v.* HYDROCHLORIC ACID.

SPIRIT OF WINE *v.* ALCOHOL.

SPIRIT VARNISHES *v.* VARNISHES.

SPIROSAL. Trade name for the glycol ester of salicylic acid $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{OCH}_2\cdot\text{CH}_2\cdot\text{OH}$. A colourless oily liquid, b.p. $169^\circ\text{--}170^\circ$, at 12 mm. Soluble in water, alcohol, and ether, and readily miscible with oils (*v.* SALICYLIC ACID and SYNTHETIC DRUGS).

SPLENIN *v.* SYNTHETIC DRUGS.

SPODUMENE (*Triphane*, Fr.). A member of the pyroxene group of minerals consisting of lithium and aluminium metasilicate $\text{LiAl}(\text{SiO}_3)_2$, and crystallising in the monoclinic system. This formula requires 8.4 p.c. of lithia, but, owing to partial replacement by potash and soda, analyses show only about 5-7 p.c. The mineral is occasionally mined as a source of lithium salts. Sp.gr. 3.1-3.2, hardness $6\frac{1}{2}$ -7. The name 'spodumene' (from *σποδοῦμενος*, something burned to ashes) has reference to the ash-grey colour shown by the common, opaque material. Transparent crystals are, however, colourless or often beautifully coloured, and are cut as gem-stones. These are strongly pleochroic; but they have the disadvantage of readily splitting, owing to the presence of a perfect prismatic cleavage. Clear yellow (rarely blue) fragments come from the gem-gravels of Brazil. Bright emerald-green crystals, coloured by a trace of chromic oxide, are found sparingly, together with beryl (emerald), in gneiss at Stony Point in Alexander Co., North Carolina; this highly-prized gem-variety is known as 'hiddenite' (or sometimes erroneously as 'lithia-emerald'). 'Kunzite' is another gem-variety of a delicate lilac or violet shade of colour, which has been found in the pegmatites at several places in San Diego and Riverside Counties in California and near Antsirabe in Madagascar. Large prismatic crystals of dull spodumene are well known from Huntington (formerly Norwich) in Massachusetts, whilst in the Etta tin mine at Harney Peak in the Black Hills of South Dakota enormous crystals, measuring as much as 47 ft. in length and with a cross-section of 3 by 6 ft., have been found; 90 tons of spodumene have been, it is said, mined from a single crystal.

L. J. S.

SPRUCE OCHRE. *Brown ochre v.* PIGMENTS.

SPRUDELSTEIN *v.* OOLITE.

SQUALENE $\text{C}_{30}\text{H}_{50}$ is a highly unsaturated hydrocarbon, isolated from shark's liver oil by Tsujimoto (*J. Chem. Ind. Japan*, 1906, 9, 958), which may be identical with Chapman's spinacene (*q.v.*), and is obtained from the liver oil of *Squalus*, *Mitsakurii*; b.p. $284^\circ\text{--}285^\circ/25$ mm., d_4^{15} 0.8596, n_D^{15} 1.4959. Forms squalene hexaozonide $\text{C}_{30}\text{H}_{50}(\text{O}_3)_6$ when treated with oxygen containing 5-7 p.c. of ozone. For derivatives,

see Riko Majima and Bennosuké Kubota (*Sci. Papers, Inst. Phys. Chem. Research*, 1922, 1, 7). Squalene is regarded as a higher aliphatic terpene, probably a dihydro-tri-terpene (*v.* SPINACENE).

By heating a mixture of squalene obtained from shark liver oil and dried Japanese acid clay under ordinary pressure good yields of a mixture of hydrocarbons were obtained. The product closely resembled natural petroleum, having a marked fluorescence, d_4^{15} 0.8279-0.8420, iodine value 18.9-21.1, C 87.58 p.c., and H 12.65 p.c. After refining with 95 and 98 p.c. sulphuric acid and fractional distillation, it had d_4^{15} 0.8054, iodine value 1.4, C 86.30 p.c., H 14.10 p.c. It is evident that the hydrocarbons consist chiefly of naphthenes, together with aromatic and unsaturated hydrocarbons. In the same way, a mixture of cholesterol, m.p. 145° , $[\alpha]_D = -22.5^\circ$, and Japanese acid clay, yielded a mixture of hydrocarbons having d_4^{15} 0.8026, iodine value 15.2, C 86.44 p.c., and H 13.50 p.c. The oil had a purple fluorescence, and a pleasant odour resembling that of petroleum; it was optically inactive. The hydrocarbons consisted chiefly of naphthenes; the lower-boiling fractions contained small amounts of paraffins (S. Kawai and S. Kobayashi, *Kôgyô-Kwagaku Zasshi*, *J. Chem. Ind. Japan*, 1923, 26, 1036; *J. Soc. Chem. Ind.* 1924, 43, B. 121).

SQUALUS ACANTHIAS LIVER OIL. A moderately clear amber-coloured liquid with a slight acid reaction; dissolves slightly in alcohol and readily in ether. At 0°C . it deposits a small quantity of white solid material. Its reactions are: with sulphuric acid, a wine-red coloration, changing to brown; with fuming nitric acid, a violet coloration, changing to green and then to brown; with hydrochloric or phosphoric acid, no coloration; when a chloroform solution of the oil is shaken with phosphomolybdic acid, a blue ring subsequently appears at the surface of separation of the two liquids; when shaken with a drop of concentrated sulphuric acid, a solution of a drop of the oil in carbon bisulphide yields a violet-purple coloration, rapidly turning brown. The character of the oil, which closely resemble those of cod-liver oil, are: sp.gr. at 15°C ., 0.9248; solidifying point, -3° to -5°C .; $n_D^{25} = 1.4761$; m.p. of the fatty acids, $33^\circ\text{--}34^\circ\text{C}$.; moisture content, 0.085 p.c.; acidity, as oleic acid, 1.7; thermosulphuric value (Tortelli), 107° ; saponification value, 0.6; acetyl value, 20; Hehner value, 94; ester value, 184. The oil contains 1.1 p.c. of squalene and 2.9 p.c. of cholesterol and other unsaponifiable constituents. It possesses the characters required in a good liver-oil for pharmaceutical uses, and it readily undergoes hydrogenation in presence of reduced nickel giving a brownish-yellow solid fat with a slight odour of tallow and having m.p. $41^\circ\text{--}42^\circ\text{C}$., re-solidification point $32^\circ\text{--}33^\circ\text{C}$., and iodine value 53 (S. Berlingozzi and M. Tomasini, *Annali Chim. Appl.* 1923, 7, 29; *J. Soc. Chem. Ind.* 1923, 561 A.).

R. Majima and B. Kubota (*Japan J. Chem.* 1922, 1, 19; *Analyst*, 1923, vol. 48, p. 400) give details of their experimental work in

connection with squalene ozonide, its decomposition products, and the dry distillation of squalene. Squalene hexaozonide decomposed in boiling water, with formation of carbon dioxide and formaldehyde, formic acid, acetone superoxide, succinic acid, lævulinic aldehyde, lævulinic acid, and two acids of unknown constitution, with empirical formulæ $C_8H_{14}O_6$ (m.p. 132° – $134^\circ C.$) and $C_6H_{10}O_5$ (m.p. 191° – $192^\circ C.$). Lævulinic and succinic acids were present in predominating quantities. Squalene is regarded as a higher aliphatic terpene, probably a dihydro-triterpene. When squalene is treated with glacial acetic acid containing sulphuric acid it is converted into a new hydrocarbon containing at least two ring structures in the molecule.

SQUILL. (*Scilla*, B. P., U.S. P.; *Scille*, Fr.; *Meerzwiebel*, Ger.)

The fleshy bulb of *Urginea Scilla* (Steinheil), a liliaceous plant found on the shores of the Mediterranean (Bentl. a. Trim. 281). It has been employed in medicine from ancient times as a diuretic and expectorant. The bulb, already dried, is imported into this country mostly by way of Malta. For an account of its collection and preparation, see Greenish, Pharm. J. 1920, 284. Under the microscope the cells of its modified leaves are seen to be loaded with mucilage, in which numerous needle-shaped or square prismatic crystals of calcium oxalate are suspended (Flück. a. Hanb. 690). The Indian squill, *U. indica* (Kunth.), is also included in the Brit. Pharm., under the title *Urginea*.

The mucilage of squill contains a *gum*, which is precipitated by basic lead acetate, an *uncrystallisable sugar* (Flück. a. Hanb.) and *sinistrin* $C_6H_{10}O_5$ (Schmiedeberg, Zeitsch. physiol. Chem. 3, 112; Ber. 12, 704), a polysaccharide present in considerable quantity. The *sinistrin* of Schmiedeberg is probably a substance distinct from the constituent of dahlia root described under the same name by Marquart (Annalen, 10, 91). After removal of the gum from squill mucilage, by treatment with basic lead acetate, milk of lime is added, when an insoluble calcium compound is formed, from which free *sinistrin* may be liberated by carbonic acid. It is purified by successive solution in water and precipitation by alcohol. *Sinistrin* is a white amorphous powder, soluble in water, insoluble in alcohol, is lævo-rotatory (cf. Kühneman, Ber. 8, 387), and does not reduce Barreswil's (Fehling's) solution. Diastase is without effect upon it, but by boiling with dilute acid it is converted into lævulose and inactive glucose. The 'scillin' of Riche and Rémont (J. Pharm. Chim. [v.] 2, 291) appears to be nearly related to *sinistrin*.

The active constituents of squill have not been obtained in a state of purity, in spite of repeated investigation, but it is certain that they closely resemble those of digitalis and strophanthus, both chemically and physiologically. Ewins (J. Pharm. exp. Therap. 1911, 3, 155) obtained two highly active constituents in a state of approximate purity, one readily soluble in water, the other, which had been obtained before, almost insoluble in water. He extracted concentrated squill tincture ($5 \times B.P.$) six times with half its volume of a mixture of chloroform (9 volumes) and alcohol

(1 volume). After washing with sodium carbonate, the combined extracts were evaporated and left a residue representing practically all the original activity. By repeated solution in hot alcohol and reprecipitation by a large bulk of dry ether this was separated into a substance soluble in alcohol and in water, but not in ether, representing one-third of the original activity, and a resinous substance, not precipitated from alcoholic solution by adding 10–12 volumes of dry ether, and almost insoluble in water.

The former constituent was an extremely bitter, yellow, non-hygroscopic and non-nitrogenous powder, readily soluble in cold water, methyl, ethyl, and amyl alcohol, acetic acid and pyridine, but almost insoluble in ether, chloroform, and ethyl acetate. With sulphuric acid it gives a brown coloration which on careful dilution passes through rose-red to a green solution, from which finally a greyish-green precipitate separates (cf. reaction for *k*- and *h*-strophanthin, *q.v.*). The aqueous solution gives no precipitate with mercuric chloride, lead acetate, or tannic acid, but the substance, like strophanthin, is salted out by ammonium sulphate. The minimum lethal dose for frogs was 1.2 mg. per kilo, about equal to that of *k*- and *h*-strophanthin and somewhat less than that of digitoxin. On hydrolysis with dilute acids the aqueous solution rapidly becomes turbid, even at ordinary temperatures, through the separation of a resinous product (cf. strophanthidin); at the same time a sugar (glucose) is formed. This water soluble substance does not seem to have been observed previously, but is almost certainly identical with *scillitin* $C_{17}H_{25}O_6$ (?) of Kopaczewski (Compt. rend. 1914, 158, 1520; Biochem. Zeitsch. 1914, 66, 501) which also yielded glucose on hydrolysis and had a lethal dose for rats of 1 mg. per kilo.

Ewins found that the resinous active principle, representing two-thirds of the total activity of squill, had a lethal dose of about 2.5 mg. per kilo for frogs, and gave with concentrated sulphuric acid and subsequent careful dilution with water a green coloration (without initial red or violet) similar to that given by digitoxin. The same substance could be obtained from commercial *scillitoxin* (Merck) by solution in alcohol and reprecipitation by ether; the original *scillitoxin* was only about half as active. *Scillitoxin* was described by Merck (Pharm. Zeit. 1879, No. 38) and is doubtless identical with *scillain* previously described by Jarmersted (Arch. exp. Path. Pharm. 1879, 11, 22). Ewins also isolated caffeine, but the amount (0.01 p.c. of the dry bulb) is too small to explain the diuretic action of squill, which seems to be due to 'scillidiuretin,' of Kopaczewski (*l.c.*), a relatively non-toxic substance causing diuresis in rabbits. 'Scillipierin' of Merck has only about $\frac{1}{100}$ of the activity of *scillitoxin*, and 'scillin' is still less active.

Although Ewins prepared the two chief principles in a purer form than his predecessors, he suggested no new names. The only ones to be retained are *scillitin*, given subsequently to the water soluble glucoside by Kopaczewski, and *scillain*, first given to the resinous one by Jarmersted.

A crystalline active principle, rather more

active than those of Ewins, is stated to have been isolated by Stoll and manufactured by Chemische Fabrik vorm. Sandoz of Basle.

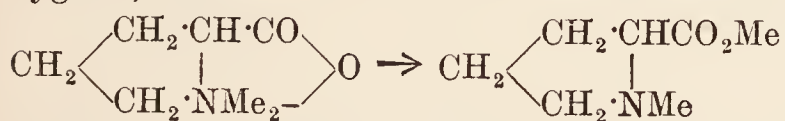
Red squill (*Urginea maritima*, Steinheil) is used as a rat poison, the raw bulb being chopped up or pulped, and the expressed juice mixed with suitable substances so as to form a bait; or an aqueous extract may be employed; or the bulb may be dried and powdered, and mixed with other materials (see Claremont, Analyst, 1922, 47, 60).

According to Garavielle and Cristol (Bull. des Sci. Pharm. 29, 29) the bulbs of *Scilla autumnalis*, fairly abundant in Languedoc, contain the same principles as *Urginea Scilla*.

G. B.

STACHYDRINE $C_7H_{13}NO_2$. *Methyl-betaïne of hygric acid*, or *dimethyl-betaïne of α -proline*, is an alkaloid which was discovered by Planta and Schulze in 1890, in the tubers of *Stachys tubrifera* (Naudin) (Ber. 1893, 26, 939). It is also the chief basic constituent of the leaves of bitter orange (*Citrus Aurantium* [Linn.]) (Jahns, *ibid.* 1896, 29, 2065), and is found in lucerne hay (Steenbock, Proc. Amer. Soc. Biol. Chem. 1916). It has been synthesised by converting ethyl hygrate into its methiodide and then treating the latter with silver oxide (Schulze and Trier, *ibid.* 1909, 42, 4654).

Stachydrine forms colourless, transparent crystals, which deliquesce in air and become opaque at 100° through loss of water of crystallisation. It melts at 210° and may be identified by its characteristic *aurichloride*, m.p. 225°, and by the fact that when heated in a glass tube the vapours evolved turn a pine splint moistened with sulphuric acid red (Schulze and Trier, Zeitsch. physiol. Chem. 1910, 67, 59). It has $[\alpha]_D^{18} -26.2^\circ$, but this value sinks to -9.2° or -9.3° if the base remains long in contact with acids or alkalis. If boiled with concentrated alkalis it is completely racemised (Deleano, Chem. Zentr. 1914, ii. 647). When heated with potash stachydrine evolves dimethylamine, and when distilled under reduced pressure it yields 66 p.c. of the isomeric methyl hygrate, thus—



together with some trimethylamine and a little hygric acid (Trier, *ibid.* 324).

The *platinochloride* (in 3 forms), the *hydrochloride*, *sulphate*, *oxalate*, *picrate*, *nitrate*, and the *ethyl* derivatives have been prepared.

For further literature on the constitution and salts of stachydrine, see Planta and Schulze, Arch. Pharm. 231, 305; Engeland, *ibid.* 1909, 247, 463; Zeitsch. physiol. Chem. 1910, 67, 403; Schulze and Trier, *ibid.* 1909, 59, 233 (*v. BETAINES*).

STACHYOSE, *Lupeose v. CARBOHYDRATES*.

STAGNIN *v. SYNTHETIC DRUGS*.

STALLOY. An iron-silicon alloy containing 3–4 p.c. of silicon, used for the construction of cores for the field and armature magnets of alternating current machinery and for the cores of transformers, principally because its magnetic hysteresis is much lower than that of pure iron. The addition of aluminium to iron has a similar effect on the hysteresis.

STANNATES. Compounds of stannic oxide with bases (*v. TIN*).

STANNIC ACID *v. TIN SALTS AND OXIDES*.

According to P. Pascal (Compt. rend. 1922, 175, 1063), magnetic analysis of the stannic acids confirms the view that they are not definite compounds (Chem. Soc. Abstr. 1923, 124, ii. 79).

STANNITE or **Tin-Pyrites** (*Zinnkies*, Ger.). A sulphide of tin, copper, and iron, or a sulphostannate, $\text{Cu}_2\text{FeSnS}_4$, which has occasionally been found in sufficient amounts to be mined as an ore of tin (27.6 p.c. Sn). The iron is often partly replaced by an equivalent proportion of zinc (0–9 p.c.). Crystals are of rare occurrence; they are scalenohedral-tetragonal, with the same degree of symmetry and very nearly the same angles as copper-pyrites (CuFeS_2), but by twinning they give rise to pseudo-cubic forms. The crystallised material is iron-black with a bright metallic lustre (sp.gr. 4.45); but the massive mineral is usually yellowish or bronze-coloured (hence the miner's name bell-metal-ore), owing to an intimate intermixture with copper-pyrites. Stannite was formerly found in some quantity in several of the Cornish tin mines (*e.g.* Wheal Rock at St. Agnes; Carn Brea), and has also been mined at Borah Creek in New South Wales and Zeehan in Tasmania. Crystallised stannite has been found in some of the silver-tin mines of Bolivia (L. J. Spencer, Min. Mag. 1901, 13, 54).

L. J. S.

STANNO-FLUORIDES *v. TIN SALTS AND OXIDES*.

STAPHISAGROINE and **STAPHISAGROIDINE**. *Delphinine* (see Vol. II. p. 486).

STAR ANISE, OIL OF, *v. OILS, ESSENTIAL*.

STAR SAPPHIRE *v. CORUNDUM*.

STARCH (Lat. *Amylum*; Fr. *Amidon*, *Fécule*; Ger. *Stärke*, *Stärkemehl*, *Farina*).

Starch, the most widely disseminated reserve carbohydrate in the vegetable kingdom, has an economic importance possessed by few other vegetable products. In some form or other, either as such or as a derivative, it enters into the dietary of man and animals to an extent exceeded perhaps by no other substance, whilst its many uses in the arts give it a prominent position in several branches of chemical industry. It is a polysaccharide usually represented in the text-books by the general formula $(C_6H_{10}O_5)_n$, in which the value of n is unknown. If starch granules, as is sometimes assumed, consist of carbohydrate substances in different degrees of hydration, the formula $(C_6H_{10}O_5)_n + H_2O$ may be employed. When the value of n is infinitely great, starch is correctly represented by this limiting formula.

1. *Occurrence*.—According to Naegeli (Die Stärke Körner, 1858) about 10 p.c. of the phanerogams possess starch-containing seeds. Even fatty seeds contain starch in the unripe condition. Of the gymnosperms and monocotyledons, about half of the members possess starch-containing tissues; of the dicotyledons only about $\frac{1}{6}$, of the division sympetalæ only about $\frac{1}{4}$. Starch is always found in great abundance in the fruits or caryopses of all the cereals, as well as of the *Leguminosæ*, in the stems of various species of *Sagus* and *Cycas*, in the roots of many plants belonging to the family of *Euphorbiaceæ* and *Zingiboraceæ*, and in the tubers of the potato, canna, and cassava.

Starch granules from different plants may in some cases be distinguished by their behaviour towards methylen-blue, naphthalene-blue, and neutral-red respectively (L. Rosenthaler, Schweiz. Apoth.-Ztg. 1923, 61, 654; Chem. Soc. Abstr. 1924, 126, i. 618).

Starch is also found under varying conditions in different parts of the same plant ; for instance, it is found as minute granules in the green leaves of most plants during the daytime, the proportion varying according to the weather and time of day. It is generally present in greatest quantity towards the evening and least in the morning, whilst during the night the starch almost or completely disappears from the leaves, especially during the summer months. Starch is also found in the pith of trees and shrubs and in the various woody tissues ; but its presence in these parts, as in the leaves, is not constant and equal, the same tissues at certain seasons being fully charged with starch and at others almost entirely devoid of it.

2. *Nomenclature.*—In this country the term ‘starch’ appears to be applied generally to that obtained from all sources, with the name of the substance from which it is prepared usually prefixed to it, such as ‘potato starch,’ ‘wheat

TABLE I.—Relative proportions of starch per cent. in various plants.

—	Krocker	O’Sullivan
Wheat . . .	53–56	54–55.5 ¹
Barley . . .	38.6–37.9	46.2–46.4
Oats . . .	27.9–36.9	35–38
Rye . . .	45–47	44–46
Maize . . .	66–67	54–58
Rice . . .	—	75–77
Buckwheat . .	44	Krocker
Millet . . .	53.7–55.5	„
Haricot beans .	37.7	„
Peas . . .	38.8	„
Lentils . . .	39.6–40	„
Potatos (air-dried)	16–23	„
Acorns . . .	64.5	Gzubata
Pollen of common pine	7.1	Von Planta
Green bananas .	12.1	Ricciardi
Soja bean . under	5.0	Meissl & Böcker
Leaves of caout-chouc tree	5.4	—
Liquorice root .	29.6	Sestini
Nasturtium officinale	2.9	Church
Tubers of yam .	25.2	Moser
Dried pears .	10.3	Bertram
„ apples .	5.2	„
Parsnips . . .	1.0	Corenwinder
Kola nuts . . .	33.7	Heckel & Schlagdenhauffen

¹ The above values appear to refer to samples containing moisture. At all events this is the case with O’Sullivan’s values. According to Ling, who has devised a new method of estimating starch in wheat and barley (J. Inst. Brewing, 1922, 28, 838), dry wheat contains 61–65 p.e. and dry barley 50–56 p.c. of starch. These values include the hemicellulose constituent which the cereal starches contain. Ling, Nanji and Harper have devised a method which estimates the amylose and amylopeetin only (see p. 394).

starch,’ ‘rice starch.’ In a few instances the affix starch is dropped, as in ‘sago,’ ‘arrowroot,’ or the product is known by some name given it in commerce, as ‘tapioca,’ ‘tous-les-mois.’

TABLE II.—Maximum diameters of the commoner varieties of starch granules.

Starch	Millimetre
Rhizomes of <i>Canna gigantea</i> .	0.175
„ „ <i>Maranta arundinacea</i> (arrowroot) . .	0.140
Tubers of potato	0.140
Broad beans	0.075
Sago	0.070
Lentils	0.067
Haricot beans	0.063
Peas	0.050
Wheat	0.050
Tubers of <i>Batata edulis</i> . .	0.045
Maize	0.030
Tapioca (<i>Jatropha manihot</i>) .	0.028
Barley	0.025
Rice	0.022
Millet (<i>Panicum miliaceum</i>) .	0.010
Buckwheat	0.009
Parsnip	0.007
Seeds of beetroot	0.004

In France the term ‘fecula’ (*fécule*) is applied to the starch obtained from roots and tubers, such as potato, manioc, arum ; from stems, such as sago ; and from fruits and seeds, as horse-chestnut, acorns, &c. ; whilst the starch obtained from all the cereals is defined as amidon or starch. Potato starch is often referred to as ‘farina.’

3. *Physical characteristics.*—In a state of purity starch presents the appearance of a white glistening powder which is tasteless and insoluble in cold water, but when it is heated with water at a temperature which varies with the different starches (see p. 347) a viscous liquid known as starch paste results. Under the microscope starch is seen to consist of granules of various forms—in most cases, however, more or less ovoid—and differing widely in size, form, and appearance, according to the source from whence they are derived. According to Payen, they may vary in size from 0.002 mm. in diameter to 0.185 mm. These wide differences are the principal means by which the various kinds of starch may be distinguished one from another as they occur in commerce (see Table II.).

It must be noted, however, that the size of the starch granules varies very considerably in different plants, being in some exceedingly minute, as in certain species of cactus ; in others, as in the potato and tous-les-mois, attaining a comparatively large size, the several granules being readily visible with a simple lens.

In the same plant—and, indeed, often in the same cell—the size of the starch granules will be found to vary, being chiefly dependent on their relative age, so that when measures of starch granules from various sources are given

they must be taken only to represent an average ; but although the dimensions of the starch granules produced by any one species of plant are by no means constant, yet none of them depart very widely from this average, and so by reference to such a standard the starch granules of different plants may readily be differentiated microscopically one from the other by an expert.

4. *Formation of starch in the living plant.*—According to Sachs starch is the first visible product of photosynthesis in the leaves of plants. In the chloroplastids it is deposited during sunlight as exceedingly minute granules which have been called transitory starch, as in this form it is hydrolysed to sugar and translocated to different other parts of the plant, there to be transformed in the leucoplastids into ordinary starch granules and other reserve carbohydrates.

There is to be seen in all starch granules a dark spot known as the hilum, which is centric in some and eccentric in others : around the hilum the various layers comprising the granules are built. The starch from a given vegetable invariably contains as above stated granules of different form and size, but these, as a rule, present a sufficiently characteristic appearance to enable the origin of the starch to be determined by a simple microscopical examination. Examined under polarised light (between crossed nicols) the granules behave as doubly-refracting crystals, exhibiting a black interference cross. This was first observed by Biot in 1844, and by Ehrenberg in 1850.

Malpighi and, more especially, Leeuwenhoeck, who lived in the seventeenth century, were the first to examine starch under the microscope. Leeuwenhoeck also studied the behaviour of starch when heated and its digestion in the animal body. Mirbel, in 1815, regarded starch as a crystalline substance ; Raspail, however, in 1826, recalled Leeuwenhoeck's observations that starch had a spheroidal form. The work of Guibourt, in 1829, and of Guerin-Vary, in 1836, was confirmatory of these observations. The question of the structure of starch granules was, however, first investigated in the most thorough manner by Fritzsche in 1834, who described their hila and stratification.

H. v. Mohl, in 1837, first proved the inclusion of starch granules within the chloroplastids. C. v. Naegeli quotes Cramer as confirming this observation, and he gives drawings of starch granules included in the chloroplastids of leaves of *Begonia* and of *Nephrolepis exaltata*. This was further confirmed by J. A. Boehm, in 1856, and by A. Gris, in 1857, the former observed also that the chloroplastids of some plants do not form starch within their substance. J. Sachs (1862–1864) stated that the production of starch is directly connected with the photolysis of carbonic acid by the chloroplastids. He showed that when green plants after having produced starch within their leaves during insolation are placed in darkness, the starch disappears from their chloroplastids to reappear by fresh photosynthesis when the plants are again illuminated.

W. Pfeffer (Monatsh. Berlin Acad. 1873, 780), and Godlewski (Flora, 1873, 378) proved that no starch is formed in the chloroplastids of plants kept in an atmosphere from which carbon

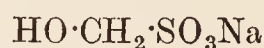
dioxide is excluded, even when they are strongly insolated. The latter observer showed, moreover, that under these conditions the chloroplastids were depleted of any starch previously present. J. A. Boehm (1874–1877) observed that a transference of some of the reserve materials, *e.g.* sugar, could in certain cases be traced to the chloroplastids of the leaf where in feeble light intensity and in entire absence of carbon dioxide there was a production of starch.

Schimper (Bot. Zeit. 1880, 881) showed that all parts of the plant (even in those which contain little or no chlorophyll) in which starch is being deposited (either as reserve or transitory starch) the granules are not surrounded by ordinary protoplasm, but are contained in or attached to certain corpuscles which are spherical or spindle-shaped. He found, moreover, that these amyloplastids are, under favourable conditions of light, converted into chloroplastids, capable of assimilating carbonic acid in the usual manner. J. A. Böhm (Sitzber. Akad. Wien, 1856, 22, 479 ; *ibid.* 1874, 69, Part I. 163 ; *ibid.* 1876, 73, Part I. 39) and A. Meyer (Bot. Zeit. 1886, 81, 105, 129, 145) showed that chloroplastids of leaves which have been depleted of their starch readily form the latter carbohydrate when they are immersed in sugar solution.

J. Sachs made some quantitative determinations in leaves of the starch formed by assimilation during the day per unit area of the leaf and that lost during the night, whilst A. Meyer (*l.c.*) proved that the chloroplastids, which are the sole organs capable of photolysing carbonic acid, are also able to elaborate starch from certain sugars. He showed that the dicotyledons produce starch more readily in their leaves than the monocotyledons, among which latter the gramineæ are included, and from his experiments he concluded that the differences in the production of starch in various leaves are not due to a relatively rapid translocation in some cases, but to lack of assimilative power. He was of opinion that starch only arises in the leaf when the starch-forming material is present beyond the requirements of nourishment and respiration. He showed that *d*-glucose, *d*-fructose, and *d*-galactose can be converted into starch by leaf parenchyma, and he stated that of the sugars just mentioned, those which are naturally present in the plant are specially favourable to starch production in the leaf. He further showed that sucrose, maltose, mannitol, and glycerol can function as starch formers.

Saposchinkoff (Ber. deut. bot. Ges. 1890, 8, 233) showed experimentally that there is more carbon dioxide photolysed than can be accounted for as carbohydrate, and he suggested that other substances are formed in the leaf by this synthesis, perhaps proteins. In this connection the recent work of Baly and his co-workers should be referred to (Trans. Chem. Soc. 1921, 1025 ; 1922, 1078 ; 1923, 185). Timiriazeff, in 1890, proved that only in presence of those rays which are absorbed by chlorophyll can the chloroplastids photolyse carbonic acid. E. H. Acton (Proc. Roy. Soc. 1890, 46, 118 ; 47, 150) concludes that apart from the photolysis of carbonic acid, green plants can only obtain their carbon normally from carbohydrates or substances closely allied to them.

T. Borkowny has shown (Ber. deut. bot. Ges. 1891, 9, 103) that when *Spirogyra majuscula* is immersed in a solution containing 0.1 to 1 p.c. of sodium hydroxymethylenesulphonate,



(which on warming with water decomposes into formaldehyde and sodium sulphite) together with disodium phosphate, starch was readily formed in the cells of this plant under conditions which precluded the possibility of the carbohydrate being formed from any other substance than formaldehyde.

Brown and Morris (Trans. Chem. Soc. 1893, 604) in a paper dealing exhaustively with the literature of the subject, and describing an elaborate series of original experiments, determined the amount of starch in certain leaves under various conditions, and plucked at different times of the day. Using the half-leaf gravimetric method devised by Sachs, they confirmed that observer's results as to the rate of assimilation, but they showed that only a small portion of this assimilated material exists at any one time in the form of starch. Their results are also opposed to the assumption of Sachs, that all the products of assimilation at some time take the form of starch. In another series of experiments the starch in leaves was estimated by hydrolysing it with diastase and determining the products of hydrolysis by means of the polarimeter and Fehling's solution. Contrary to Wortmann's statement (Bot. Zeit. 1890, 581, 597, 617, 633, 657), Brown and Morris showed that leaves contain sufficient diastase to transform far more starch than they can have contained at any one time, and that it is this diastase which effects the solution and translocation of the leaf starch. They further showed that any conditions which favour a decrease in the leaf starch result in an increase in leaf diastase; e.g. leaves kept in darkness either attached to the plant or otherwise exhibited a marked increase in diastatic activity. In view of their previous studies on the germination of graminaceous seeds (Trans. Chem. Soc. 1890, 458), Brown and Morris explained this increase in diastase by the assumption that as long as the conditions favour assimilation, the leaf cells are supplied with a larger quantity of newly-assimilated materials in the form of various sugars than they can make use of or translocate. At this period, they state, there is little or no elaboration of diastase by the cell protoplasm, probably none at all in those cells in which starch deposition is actually proceeding. When the light fails and assimilation falls off, the cells speedily use up or translocate the excess of assimilated products, such as sucrose, and they begin to draw upon the more permanent reserve, starch, for which purpose diastase is needed, and this enzyme is elaborated by the somewhat starved protoplasm. Brown and Morris concluded, therefore, that the secretion of diastase, whether by the leaf cell or by the embryo of the grasses, is to some extent a phenomenon of starvation. In the leaves of *tropaeolum* they found the sugars present to be sucrose, dextrose, lævulose, and maltose. Sucrose is, according to them, the first sugar to be synthesised by the assimilatory processes; it is said to accumulate in the cell-sap of the leaf parenchyma when

assimilation is proceeding vigorously, and when the concentration exceeds a certain point starch commences to be formed from it by the chloroplastids, which latter carbohydrate, as already stated, is only drawn upon when the more readily metabolised sucrose has been partially used up. It is interesting to note that in their paper on the germination of the gramineæ, Brown and Morris (*l.c.*) pointed out that sucrose is the most readily assimilated by the germ of all the sugars.

It has been shown by F. Boas (Biochem. Zeitsch. 1917, 78, 308) that moulds (*aspergillus* and *penicillium*) when grown in 5–10 p.c. sugar solutions in presence of 1–5 p.c. of ammonium salts at temperatures varying from 30° to 37° produce a substance giving a blue iodine reaction both in the mycelia and in the culture medium. Positive results were obtained with dextrose, lævulose, and sucrose, but not with lactose or maltose. One of the writers of this article (A. R. Ling) has confirmed this observation working with *Aspergillus niger*, and he finds that in addition to dextrose, lævulose, and sucrose, the substance giving the blue iodine reaction is also formed from galactose. Whether the substance giving the blue iodine reaction is actually starch as assumed by Boas remains at present unproven.

H. Pringsheim and K. O. Miller (Zeitsch. physiol. Chem. 1922, 118, 236) show that when *Spirogyra dubia*, previously freed from starch, is allowed to act on glycerol, dextrose, lævulose, galactose, maltose and cellobiose starch is formed. Negative results were obtained with the polyamyloses.

5. *Starch granules*.—According to C. v. Naegeli, in 1858, starch granules consist of two substances—granulose, the principal constituent (which gives the well-known blue coloration with iodine), and starch cellulose. Starch cellulose is said to give a yellowish coloration with iodine, but after treatment with sulphuric acid or zinc chloride a blue coloration with the same reagent. Boiling water is said to convert it largely into soluble starch. Naegeli put forward the hypothesis that the granules do not grow like crystals from within outwards (by apposition), but from outwards to within (by intussusception). According to this view a layer of starch is first deposited round the inner surface of the amyloplastids, which latter are presumably kept filled with a solution of the starch-forming substance. Another layer is then deposited inside the first, and so on until the cell is completely filled. Assuming this hypothesis to be correct, the outside layer of the granule is the oldest, and the portions near the hilum the most recent and the richest in water. On the other hand, A. Meyer (Die Stärke Körner, 1895) holds the view which he supports experimentally, that starch granules are built up within the amyloplastids like crystals by apposition, and that the layers are formed of radially-arranged aggregates of sphæro crystals. The well-known double refraction of starch granules above referred to is confirmatory of Mayer's views of their structure. The radial arrangement of the sphæro crystals can sometimes be seen in the fresh starch granules, thus in the case of sorghum starch, it can be made clear after treatment with a

concentrated solution of calcium nitrate (Meyer), and the same is true of maize starch after boiling with chloroform and a little chromic acid (Buscalioni, 1891).

Meyer points out that during the period of full vital activity of the plant, the included starch granules are enveloped in amyloplastid substance, and this was confirmed by Salter's observations in 1898. Meyer believes that the substance of the granules consists of a mixture of so-called α - and β -amylose¹ with amylo-dextrin (W. Nägeli, Ann. 1874, 173, 218; Brown and Morris, Trans. Chem. Soc. 1889, 449). C. v. Nägeli drew attention to the occurrence of starch granules which give a red coloration with iodine in the seed envelope of *Chelidonium majus*, and Gris (1860) in those derived from the endosperm of a certain variety of rice. The occurrence of starch granules giving a red coloration with iodine is discussed at length in Meyer's monograph.

Meyer describes minutely how centric and eccentric granules are built up within the amyloplastids. It has been pointed out by Naegeli that several starch granules are sometimes formed in one amyloplastid, and these Meyer denotes as adelphous granules—oligo-adelphous or polyadelphous—according as few or many granules occur in one amyloplastid.

Reverting to C. v. Nägeli's observation that starch granules consist of a mixture of granulose and starch cellulose, it should be mentioned that Brown and Heron, in 1879, treated potato starch paste of known concentration with malt extract in the cold for 4–8 minutes and determined the weight of the insoluble precipitate which they regarded as starch cellulose. They found that the amount varied from 2.0 to 4.5 p.c., according to the previous treatment of the starch with potash solution. Meyer points out that by freezing starch paste as much as 30 p.c. on the starch of insoluble matter may be obtained. This becomes understandable in the light of the observations of Maquenne and Roux (*see also* Ling and Nanji, p. 365). Brown and Heron observed that their supposed starch cellulose existed in two forms, one being readily converted into soluble starch by boiling water and the other not.

Within recent years the study of the composition of starch granules has been taken up by French chemists, notably by Maquenne and Roux. From their experiments they have arrived at the conclusion that far from starch cellulose, or as they term it amylocellulose, or amylose, being in a sense an extraneous constituent of starch granules, it forms in different states of condensation the principal constituent. Their view is that 80–85 p.c. of the natural starches consist of amylocellulose in association with another substance to which they give the name amylopectin. It is asserted that the viscosity of starch paste is due to this substance.

Madame Gatin-Gruzewska (Compt. rend. 1908, 146, 540) has devised a method for the

¹ These are purely hypothetical substances and have never been isolated. α - and β -amylose are assumed to differ from one another by their degree of hydration. The former is said not to be immediately liquefied by boiling water, but by prolonged boiling is slowly converted into the latter which dissolves at once in boiling water.

isolation of amylopectin. It consists in treating potato starch (10 grms.) with 1 p.c. soda solution (500 c.c.). The liquid is subsequently neutralised with acetic acid and diluted to one litre. Under this treatment the amylopectin which forms the envelope of the granules is said to swell up, the amylose contained within the envelope taking up water, and the envelope bursting as a result of osmotic pressure developed within itself; the amylose solution it is said is thus liberated. When neutralised with acetic acid, the envelope is said to contract and the separation of amylose and amylopectin is rendered complete. When an equal volume of water is added after 24 hours the empty amylopectin envelopes settle to the bottom of the vessel, the supernatant liquid consisting of amylose solution. In this way it was found that the amount of amylopectin in starch is 40–45 p.c. The amylopectin envelope is said to consist of a series of sacs fitting into one another. Alkalis convert the sacs into a finely granulated filamentous substance, which when treated with an excess of alkali and water and then neutralised give an opalescent solution. The specific rotatory power of the dissolved matter in such a solution ($c=0.178$) is $[\alpha]_D +221^\circ$. These solutions of amylopectin give a purplish-blue iodine reaction which is much less intense than the clear blue iodine reaction obtained with solutions of amylose.

Maquenne (Compt. rend. 1908, 146, 542) states that the amylopectin isolated by Gatin-Gruzewska was impure and still contained amylose insoluble in boiling water. He holds the view that amylopectin and amylose cannot be regarded as homogeneous, but must consist of a complex mixture of homologous or differently condensed products. There is a likelihood that in the natural formation of the starch granule the amylopectin is derived from amylose by condensation just as amylose is derived from sugars. This gradual transition would explain the difficulty of separating these two substances, as there appears to be no sharp transition between the group of slightly soluble amyloses occupying the end of the series, and that of the least resistant amylopectin.

Maquenne and Roux (Ann. Chim. Phys. 1904, [8] 2, 109; 1906, [8] 9, 179) have obtained artificial starch granules consisting exclusively of amylose by the following method: A starch paste was kept at a low temperature for a week, and the substance which deposited was successively collected and washed with cold water. It was then twice heated with water at 120° and subsequently after each treatment submitted to the action of malt extract at 56° until the iodine reaction disappeared. The residual substance was again collected, washed, and dried over sulphuric acid, when it was obtained as a hard granular mass containing about 1.5 p.c. of siliceous ash and a little nitrogenous matter derived from the malt extract: it did not give an iodine reaction, and was practically insoluble in water at 120° , but dissolved at about 150° – 155° , when the temperature was raised by degrees; the solution gave a blue coloration with iodine. When a solution, obtained by heating as just described for 10 minutes, was allowed to cool it became viscous, and finally

the whole was converted into a gelatinous mass. If, on the other hand, the heating were continued for more than an hour a perfectly clear solution was obtained which slowly deposited granules resembling those of natural rice starch. These artificial granules are said to consist of pure amylose; they did not give a paste with hot water, and they dissolved in alkalis without previous swelling. Unlike the granule of natural starch they were insoluble in boiling water, and they did not give a coloration with iodine.

These characteristics are explained by the assumption that the artificial granules consist of amylose in a more highly condensed state than it exists in the natural starches, which it is assumed contain the same amyloses together with less highly condensed forms playing the rôle of solvents towards the higher members. It is thus seen that the so-called starch cellulose of Naegeli and others does not of necessity exist in the granules to the extent indicated by the published values of Brown and Heron, as this substance can be formed as shown above by the reversion of starch paste or of starch solution. At the same time Maquenne (*l.c.*) believes that starch granules are analogous in composition with starch paste which has been prepared for some time, *i.e.* they consist of reverted starch—a mixture of amyloses in various states of condensation. Fernbach and Wolff (*J. Inst. Brewing*, 1904, 10, 216) have pointed out that amylocellulose is formed by the action of a coagulating enzyme, amylocoagulase, on a solution of starch. This enzyme has been found in various seeds and in ordinary kilned malt. It may have much to do with the deposition of starch within the amyloplastids.

A. Fernbach (*Ann. Brass. et Dist.* 1908, 11, 481) is of opinion that solid starch should be regarded as a coagulated substance, which in nature has probably passed from the state of apparent solution to the solid form, and all the changes that starch can undergo without chemical alteration should be regarded as changes of this or the opposite kind. The conversion of solid starch into starch-paste or into so-called soluble starch is, in a sense, a change of the latter kind; the partial reversion of starch-paste to a solid substance is a change of the former kind. Attention is drawn to the fact that natural starches, like malt extract, are acid to phenolphthalein and alkaline to methyl orange, and he considers that the properties of starch depend almost exclusively on the nature and proportion of the accompanying mineral substances. These conclusions are based on the results of his investigation on amylocoagulase, the enzyme present in cereals which coagulates starch-paste, which he found to have a maximum activity in a medium which is neutral to phenolphthalein.

Fernbach has shown (*Compt. rend.* 1904, 138, 428) that potato starch granules, especially the light ones, contain a nucleus relatively rich in phosphorus, on which is superposed so as to form the large granules layers of starch free from phosphorus.

6. *Properties.*—Starch is insoluble in cold water, alcohol, ether, or any other known solvent. Ordinary air-dried starch usually

contains about 18 p.c. of water, which may be entirely driven off by heating for some time in a current of dry air at a temperature of 100°–105°. Under these conditions starch appears to be a most highly hygroscopic substance, which rapidly absorbs moisture from the air until it regains its original 18 p.c.; if exposed to a damp atmosphere it is capable of absorbing as much as 35 p.c. of moisture.

The specific gravity of air-dried starches varies considerably, the variation being mostly due to the moisture content. Starches that have been freed from water have not absolutely the same specific gravity, anhydrous potato starch having a value 1.650, and anhydrous arrowroot starch 1.5648.

7. *Action of heat.*—Freed completely from moisture, starch may be heated to a temperature of 160° without undergoing any change; at temperatures higher than this it becomes coloured, and is partly converted into dextrin. If, however, ordinary air-dried starch be heated to 160° it quickly undergoes decomposition, becoming converted to a greater or less extent into dextrin and reducing sugars, the action varying with the particular kind of starch used (*v. DEXTRINS*).

Experiments have been made by J. and H. Heron as to the effects of heat on different varieties of starch. Potato, sago, and rice were heated to 190° for two hours, cooled, dissolved in cold water, and the specific rotatory powers of the solutions taken. Potato and sago starch were entirely decomposed under these conditions, and their solutions showed a specific rotatory power of $[\alpha]_D = 154.3$ for potato, and $[\alpha]_D = 193.3$ for sago; rice starch appears to offer great resistance to the action of heat, being only partially decomposed at the above temperature.

According to Schubert (*Monatsh.* 1884, 472), the starch granule, under the influence of high temperature, is altered in such a manner that those layers which are rich in granulose are at once converted into soluble starch and dextrin, whilst the principal portion of the layers rich in cellulose only undergo this transformation after a time. When starch which has been subjected to a high temperature is treated with cold water, the soluble starch, dextrin, and other products of decomposition pass into solution, and an organised residuum is left, which resembles the form and structure of the original granule, and contains small quantities of unchanged granulose.

By dry distillation starch yields carbon dioxide, gaseous hydrocarbons, water, acetic acid, and empyreumatic oil, and leaves a porous cinder.

On distilling dry starch with lime in the proportion of 1 to 4 it yields acetone, mesityl oxide, a series of ketones, and various condensation products of acetone (*Horvat, Chem. Zentr.* 1887, 38).

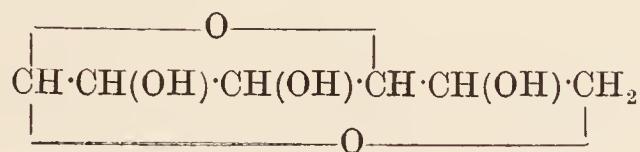
By distillation with manganese dioxide and dilute sulphuric acid it yields carbon dioxide, aqueous formic acid, and furfural.

In the open fire it softens, swells up, evolves choking vapours, and finally burns with a bright flame.

Distilled with hydrochloric acid and man-

ganese peroxide, it yields, among other products, trichlorinated acetic aldehyde and pentachlorinated propionic aldehyde.

According to A. Pictet and J. Sarasin (Compt. rend. 1918, 166, 38), when starch is heated gradually under a pressure of 12–15 mm., the fraction distilling between 200° and 300° amounts to about 45 p.c. of the original carbohydrate. Crystals have been separated from it which appear to be identical with Tanret's lævogluosan (β glucosan) $C_6H_{10}O_5$. Pictet and Cramers' (Helv. chim. Acta, 1920, 3, 640) show that it has the constitution



< 1, 4 > — (1, 6) anhydroglucose

When starch is brought in contact with hot water the granules, owing to a large absorption of water, swell up enormously; and, at a temperature varying according to the variety of starch, ultimately rupture, forming a viscous liquid which is known as 'starch paste.'

The different varieties of starch gelatinise with hot water at very different temperatures, as is seen in the following table by Lintner (Brauer und Malzer Kalendar, 1889), which gives the temperatures of complete gelatinisation for the commoner varieties of starch:—

TABLE III.

Starch from	Temperature at which complete gelatinisation takes place
Potato	65°C.
Maize	75°C.
Barley	80°C.
Wheat	80°C.
Rye	80°C.
Rice	80°C.
Kilned malt	80°C.
Green malt	85°C.
Oat	85°C.

This table gives the temperatures at which the various starches gelatinise completely in the pure state. In the crude condition a much higher temperature is necessary.

Under the action of boiling water the starch granules do not all swell up and burst at once—the smaller being attacked first, the older last. This progressive action of heat can be very well observed when potato starch has been suspended in 12–15 times its weight of water, and gradually heated on the water-bath; hardly any change is apparent up to 55°; at 57° the smaller granules begin to show signs of rupture, and as the temperature rises this process of swelling and bursting of the contents through the outer wall of the granule goes on increasing, the earliest-formed granules being the last to give way, until, at a temperature between 65°–70°, a thick viscous liquid, of uniform consistency, is obtained.

On cooling, starch paste contracts and

becomes, when very thick, a firm solid mass, which, after standing a short time, cracks; its maximum contraction is reached at the freezing-point, when a separation of the water and starch takes place to a certain extent. When the temperature is raised, the water which had been frozen out does not again combine with the starch, and may be drained away, whilst the consolidated starch paste remains as a felty mass which, when dry, has the appearance of mother-of-pearl (Payen).

Wide differences in the viscosity of this paste are observed, depending not only upon the variety of starch employed, but also upon the treatment to which the starch is subjected during the processes of purification and drying.

According to Brown and Heron (Chem. Soc. Trans. 35, 596), starch which has been treated with dilute potash and acid in the process of purification produces a paste of less viscosity than the same starch which has not been so treated; they also find that great variations in the consistency of the resulting paste are produced by slightly altering the manner of drying.

These facts are of importance, seeing that the technical value of a starch in certain industries depends entirely upon the viscosity produced by it when acted upon by boiling water.

Potato starch is used in large quantities for sizing and stiffening yarn and cloth, so that it is of importance to the manufacturer to obtain that sample of starch which will make the stiffest cloth and which has the greatest tenacity. In order to determine this, the following method has been recommended by O. Saare and P. Martens (Zeits. Spiritusind, 1903, 26, 436–437). An immersion body is constructed of a circular brass plate, 22 mm. in diameter, to which a brass wire is fixed vertically at the centre, having a mark at a distance of 3 cm. above the disc and terminated by a hook at the top. The starch paste is prepared by weighing out 7 grms. of starch into a beaker of 200 c.c. capacity provided with a small metal spoon. The whole is tared, and 164 c.c. of boiling water are added with continuous and gentle stirring all the time. This may be effected either immediately or after immersion in a boiling water-bath for 2, 5, or 10 minutes. This spoon is then removed and the brass disc supported by a clamp is immersed in the paste exactly up to the mark; 10 c.c. of olive oil are poured over the surface to prevent the formation of a hard skin by evaporation, and the whole is left at rest for 20 hours at a temperature of about 17.5°. A hand balance, one of the pans of which has been replaced by a counterpoise, is attached to that of the disc. On the other scale pan an uninterrupted stream of sand is discharged at a uniform rate of about 9 grms. a minute, until the disc is torn from the paste. The weight of the sand is then taken as a measure of the stiffness of the paste. Experiments showed that the time during which the paste was heated at the boiling-point had a considerable influence on the results. Certain starches, especially those with a high gelatinising-point, such as wheat and maize starches, did not attain their maximum stiffness until they had been boiled for several minutes; on the other

hand, certain potato-starch pastes had a maximum stiffness without heating, any heating beyond that necessary to produce the maximum stiffness, caused a rapid decrease in stiffness. The values of the various samples showed a tendency towards equalisation by prolonged heating.

H. Cappenberg (Chem. Zeit. 1910, 34, 218–220) has designed a viscosimeter for starch pastes in which a spherical weight of standard dimensions is drawn upwards through a column of the paste of fixed height and temperature, the time occupied in doing this, under the pull of a known load in grams, being noted. A series of trials are made with a regularly decreased load, these being tabulated for comparison, as single observations with a fixed load are useless for this purpose. In comparing starches it was found that pastes containing 5 p.c. of potato starch and 9 p.c. of wheat starch gave identical values, and it may reasonably be assumed that for these samples the thickening powers were in that ratio.

Erwen (J. Soc. Chem. Ind. 1907, 26, 501–502) makes solutions in the cold with the help of sodium hydroxide, and determines their viscosities in a Redwood viscosimeter. The weighed sample of starch is shaken continuously with 230 c.c. of cold water, and 15 c.c. of a 10 p.c. solution of sodium hydroxide with the addition of enough water to bring the whole up to 250 c.c., until the solution begins to thicken. It is allowed to stand until the next morning before measurement. When close attention is paid to constancy of procedure the method is claimed to give concordant results with the same starch, whilst different starches and different brands of the same starch are easily differentiated.

The sp.gr. of starch paste, as determined by Brown and Heron, is 1.66 at 15.5°. Starch paste is strongly dextro-rotatory, but, owing to its opacity, the determination of the specific rotatory power is very difficult. The mean of Brown and Heron's observations at a concentration of 1 grm. per 100 c.c. is $[\alpha]_D^{20} = 208^\circ$, but the accuracy of this value is not to be relied on.

8. *Soluble starch*.—Under certain conditions starch undergoes a peculiar modification, by which it is rendered completely soluble in hot water from which it can be precipitated as a brilliant white flocculent substance by alcohol, or if the solution be somewhat concentrated and allowed to stand some time a white granular precipitate slowly separates out. Under these conditions, the precipitate is always found by microscopic observation to be made up of minute particles, entirely without structure and without action on polarised light. Lintner found, however, that when a dilute solution is submitted to a low temperature, it is possible to obtain this precipitate in the form of sphaerocrystals.

When starch paste is largely diluted with water and boiled for some considerable time, a portion of it goes into solution and may be easily filtered off. A similar reaction may be brought about more rapidly if starch with about ten times its weight of water be heated under pressure up to 130°–150° (Stumpf, Bied. Zentr. 1880, 457). Under these conditions the greater

portion of the starch is rendered soluble, and corresponds to the solutions of Maquenne and Roux's so-called amylose which enters into solutions at this temperature.

The same effect may be brought about by treating potato starch at the ordinary temperature with a solution of hydrochloric acid of specific gravity 1.037 for 7 days (Lintner, J. pr. Chem. 1886, 34, 378); the starch granules are then washed until free from acid, and on treating with boiling water, dissolve completely without the production of the usual viscous paste. This extraordinary change in the properties of the granules is not accompanied by the slightest change of structure, the granules having the same appearance under the microscope both with ordinary and polarised light.

Soluble starch may be prepared, according to O'Sullivan, as follows: Starch paste is acted on with the least possible quantity of the cold water extract of malt, previously heated to 75° for 30 minutes, or with diastase solution, or with dilute sulphuric acid (sp.gr. 1.120) at 75°, and further action stopped as soon as limpidity is produced by raising the liquid quickly to the boiling-point if diastase or malt extract be employed, or by adding barium carbonate if sulphuric acid has been used, until neutrality is produced. The liquid is then filtered and evaporated until a slight skin begins to form on the surface; when the soluble starch falls out on cooling as a brilliant white precipitate. This is allowed to rest for a few days, and then treated with cold water, with which it is washed well upon a filter. It is purified by dissolving it in as small a quantity of boiling water as possible, and again filtering, if necessary using a hot-water funnel. On cooling, the soluble starch separates from the filtrate as before.

Perhaps the readiest way of preparing soluble starch is that recommended by Zulkowski (Chem. Zentr. 1888, 1060), who finds that starch dissolves in hot glycerol and is converted into the soluble modification; this, in turn, if the action be continued, becoming transformed into erythrodextrin and achroodextrin, with the production at the same time of reducing sugars. 60 grms. of dry-potato starch are heated for half an hour with 1 kilo. of glycerol at a temperature of 190°, then cooled down to 120°, and the soluble starch precipitated by the addition of two or three times its volume of strong alcohol. If necessary, the precipitate may be further purified by dissolving again in the smallest possible quantity of boiling water, and reprecipitating therefrom with 90 p.c. alcohol.

Soluble starch has been prepared by treating starch granules with a 1 p.c. solution of caustic soda (Wroblewski, Ber. 1897, 30, 2108); and Syniewski has also prepared it by treating potato starch suspended in water with sodium peroxide (*ibid.* 1897, 30, 2415). This product is soluble in cold water up to 12.5 p.c., and dissolves in hot water in any proportion. Soluble starch prepared in this way, however, appears to differ from that prepared according to Lintner's method.

A. Reychler (Bull. Soc. chim. Belg. 1923, 221) prepares soluble starch by treating 100 parts of potato starch with 0.75 part of potassium dichromate in 130–150 parts of *N*/4-

hydrochloric acid. After 20 hours the dichromate is reduced by a trace of sulphurous acid or sodium sulphite, the starch collected and washed several times. An alternative method is to use potassium permanganate, but the author prefers the dichromate method.

Soluble starch prepared by the methods of Lintner and O'Sullivan, when in solution, rotates a ray of polarised light strongly to the right. Brown and Morris find its specific rotatory power to be $[\alpha]_{\text{D}3.86} + 216^\circ$, $[\alpha]_{\text{D}3.86} + 195^\circ$. Lintner gives it as $[\alpha]_{\text{D}} + 200^\circ$, and Brown, Morris, and Millar give a value in 2.5–4.5 p.c. solutions at 15.5° of $[\alpha]_{\text{D}} + 202^\circ$.

E. Fouard has carried out some interesting investigations with regard to starch solutions and soluble starch, but space does not permit any further description (*cf.* Compt. rend. 1908–1909; Seventh Internat. Cong. App. Chem. 1909).

Soluble starch has no action whatever on Fehling's solution, and, like starch paste, its solution is coloured an intense blue with iodine.

Chloramine-T, or *p*-toluene sodium sulphochloramide, may be used with 1 p.c. of the substance mixed with starch which causes the latter to become soluble. The mixture is boiled with water, when a perfectly translucent starch solution is formed, which can be used at once for the customary processes in textile manufacture. The use of this agent has the advantage of degrading the starch molecule only very slightly, no dextrin or sugar being formed. It gives the usual deep blue coloration with iodine (*Chem. Trade Journ.* May 16, 1924, 591; *Pharm. J.* 1924, 113, 67).

9. *Action of alkalis.*—When a moderately-strong solution of potassium or sodium hydroxide is added to starch paste, the previously opalescent liquid is rendered perfectly transparent. This increase in transparency is due to the solution of the suspended starch cellulose by the alkali. The specific rotatory power is at the same time considerably lowered, but resumes its original value if the alkali be neutralised by acetic acid. These facts point to the production of a definite compound of starch with potash or soda. An interesting feature in this reaction is that, after acidification, the solution remains transparent, and possesses all or nearly all the viscosity of the original starch paste (Pfeiffer and Tollens, *Annalen*, 1882, 210, 285; Brown and Heron, *Trans. Chem. Soc.* 35, 596).

When starch is treated with an alkaline solution the granules swell up and form an exceedingly tough viscous mass, which readily dissolves in water, forming a solution in no way differing from that produced by the action of alkali on starch paste.

Symons (*Pharm. J.* [iii.] 13, 237) has investigated the process of swelling of starch granules under the action of heat at different temperatures, and of alkaline solutions of varying strengths, and concludes that the process of swelling through the action of these widely-differing agents is one and the same, and, as a result of his experiments, proposes a method whereby the several varieties of starch may be detected by their behaviour with dilute alkaline solutions of definite strength.

The most suitable are solutions of caustic

soda of 0.5–1.5 p.c. 0.1 grm. of the starch is repeatedly stirred up with 1 c.c. of the particular soda solution, and, after 10 minutes, examined under the microscope.

P. Karrer (*Helv. Chim. Acta*, 1921, 4, 811) finds that solutions of α -di, α -tetra, β -hexa, and α -octa-amyloses (see pp. 361–363) in dilute aqueous sodium hydroxide contain additive compounds, which are precipitated by alcohol, and after purification by solution and reprecipitation respectively correspond exactly with the formulæ $\text{C}_{12}\text{H}_{20}\text{O}_{10}\cdot\text{NaOH}$, $(\text{C}_{12}\text{H}_{20}\text{O}_{10}\cdot\text{NaOH})_2$, $(\text{C}_{12}\text{H}_{20}\text{O}_{10}\cdot\text{NaOH})_3$, and $(\text{C}_{12}\text{H}_{20}\text{O}_{10}\cdot\text{NaOH})_4$. Polymeric anhydro-sugars, as internal acetals, therefore combine with one molecule of sodium hydroxide per molecule of anhydro-sugar, and so permit the determination of the molecular weight of this. Thus hexa-amylose is a polymeric maltose anhydride, inulin is probably derived from anhydro-difructose, and xylan from anhydro-dixylose. In further confirmation of previous results, a compound $(\text{C}_{12}\text{H}_{20}\text{O}_{10}\cdot\text{NaOH})_x$ was obtained from soluble starch. It is suggested that such polysaccharides are crystalline substances, of which the lattice points are occupied by polymeric molecules, which in the case of starch are complexes, $(\text{C}_{12}\text{H}_{20}\text{O}_{10})_2$ or $(\text{C}_{12}\text{H}_{20}\text{O}_{10})_3$. The forces of valency by which the polymeric molecules are fixed in the crystal are so strong that the resulting 'crystal-polymerisation' very closely resembles true polymerisation. If the forces in question approximate in strength to those responsible for the existence of the polymerides, and also to those operating in the anhydro-sugar, it will be extremely difficult to isolate intermediate degradation products. This is probably the case with cellulose.

Ammonia solution, either dilute or concentrated, has no action whatever on starch or on starch paste.

If a trace of starch be added to a solution of a salt of ammonia, and then a solution of sodium hydroxide drop by drop, the starch remains unchanged until the whole of the ammonia salt has been decomposed; but the least excess of soda causes immediately an expansion of the starch granules.

Tables IV. and V. give the results of Symon's experiments for various starches.

TABLE IV.—*Action of heat on starch granules.*

Variety of starch	Order of relative size of granules	Few granules swollen at	Majority of granules swollen at	All granules swollen at
		°C.	°C.	°C.
Potato .	2	55	60	65
Cassava .	7	58	63	68
Natal .	4	58	65	70
Wheat .	5	60	65	70
Tous-les-mois	1	65	68	72
Bermuda .	4	62	69	73
Sago .	3	64	68	74
Maize .	6	65	70	77
Oat .	8	65	70	77
St. Vincent .	4	66	73	77
Rice .	9	70	75	80

Starch exhibits a peculiar reaction with ammoniacal copper solution. Dry starch readily absorbs cupric oxide from ammonio-cupric oxide solution, and decolorises the liquid, the action being more rapid if the starch has previously been slightly moistened. Starch paste acts in a similar manner. A deep-blue compound is formed, from which water, and even dilute ammonia, remove only traces of copper. Repeated washing, however, with strong ammonia eventually removes every trace of copper (Guignet, *Compt. rend.* 109, 528).

Dilute hydrochloric acid immediately decomposes this compound, forming cupric chloride, which may be readily removed by washing with water, leaving the starch granules intact.

After prolonged digestion with strong ammonia in the cold, the granules swell up and become converted into the soluble modification,

On heating the compound of cupric oxide and starch with water at 80° the starch gelatinises, forming with the cupric oxide a beautiful blue viscous liquid.

Starch possesses the property of combining with other bases than sodium and potassium hydroxides. If to the transparent colourless jelly formed by acting on starch with sodium hydroxide, a 7 p.c. aqueous solution of calcium chloride be added, double decomposition takes place, and a thick, white, insoluble mass is formed, which is a compound of starch with calcium chloride. A series of compounds of starch with other bases may similarly be formed, in which the starch cannot be detected by means of iodine. The starch in such compounds is, however, immediately set free by acids (Payen).

TABLE V.—*Action of dilute NaHO on starch granules.*

Variety of starch	Order of relative size of granules	Few granules swollen with	Majority of granules swollen with	All granules swollen with
		p.c.NaHO	p.c.NaHO	p.c.NaOH
Potato .	2	0·6	0·7	0·8
Oat .	8	0·6	0·8	1·0
Natal .	4	0·7	0·8	1·0
Tous-les-mois	1	0·7	0·9	1·0
Wheat .	5	0·7	0·9	1·0
Bermuda .	4	0·8	0·9	1·1
Sago .	3	0·8	0·9	1·1
Maize .	6	0·8	1·0	1·1
Cassava .	7	0·8	1·0	1·1
St. Vincent	4	0·9	1·0	1·2
Rice .	9	1·0	1·0	1·3

Starch is completely precipitated from a dilute aqueous solution by a solution of lime in sugar-syrup. The composition of the precipitate varies according to the quantity of lime added. With baryta and strontia water similar compounds are formed (C. J. Lintner, *Zeitsch. angew. Chem.* 1888, 232).

10. *Action of acids.*—A swelling of the starch granules, similar to that occasioned by sodium or potassium hydroxide, is produced immediately by all mineral acids, and by some organic acids, e.g. tartaric and citric acids, after being in con-

tact for some time. No swelling is produced by acetic or oxalic acids, no matter how concentrated their solutions may be.

When air-dried starch is trituated with concentrated sulphuric acid considerable heat is evolved, and, after a short time, complete carbonisation takes place. If, however, the starch be previously freed from moisture, on addition of the acid the granules swell up and form certain mucilaginous compounds, which are soluble in water, and rotate a ray of polarised light strongly to the right. When boiled with alcohol they lose all the sulphuric acid, leaving a modified form of starch. Upon neutralising the aqueous solution with bases, uncrystallisable salts are formed (Hönig and Schubert, *Monatsh.* 6, 768).

When diluted sulphuric acid 1 : 2 to 1 : 4 is added to air-dried starch, a swelling up of the granules takes place, and the mass becomes thick and viscous. On standing some hours the viscosity disappears, the iodine reaction showing the presence of soluble starch only; but on standing for some days this becomes gradually hydrolysed to maltose, and finally to dextrose.

Nitric acid yields with starch various products, depending on the strength of the acid, temperature, and duration of the action.

When starch is boiled for some time with moderately concentrated nitric acid (sp.gr. 1·200) it is completely converted into oxalic acid. Cold concentrated nitric acid (sp.gr. 1·520) added to starch causes the granules to swell up, first into a viscous mass, which after a short interval becomes quite limpid; if now water be added to this solution, according to Braconnot (*Annalen*, 7, 245), a white powder is precipitated which when dry explodes on being struck.

If, however, the solution of starch in nitric acid be kept, water precipitates less and less of the nitrate, and at last none, whilst a substance resembling saccharic acid remains in solution (Pelouze, *Compt. rend.* 7, 713).

When starch is heated with a mixture of nitric acid and fuming sulphuric acid containing some 2–3 p.c. of SO₃ at a temperature of 45°–50° a starch nitrate having a formula C₁₂H₁₂(NO₂)₈O₁₀, and containing about 16·5 p.c. of nitrogen, is formed. It is an orange-coloured highly explosive powder, and is soluble in ether-alcohol.

Strong hydrochloric acid added to dry starch causes the granules to swell, and in a very short time to become a thick, semi-translucent, viscous mass. If to this a large quantity of cold water be added, a milky fluid results, which consists entirely of the soluble modification. If, however, the swollen mass be allowed to remain for a few days, the soluble starch will be found to have entirely disappeared, whilst at the same time the viscous mass becomes perfectly limpid, and separates into two layers, the lower one consisting of the products of hydrolysis of the granulose—namely, achroodextrin, maltose, and dextrose—whilst the upper layer consists exclusively of ‘starch cellulose.’

If, however, the action of very dilute (1–2 p.c.) mineral acids, such as sulphuric or hydrochloric acid, upon ungelatinised starch in the cold be allowed to continue for some considerable time (two months or more), the granules gradually

become disintegrated, a portion becoming converted into dextrose and going into solution, whilst the residual substance retains little or nothing of the original form of the starch granule. Concurrently with these changes, the iodine reaction undergoes considerable modification, the original deep-blue colour gradually giving place to purple, and this, through reddish-purple and reddish-brown, to a pale yellowish-red, which is not further modified, even if the starch remain in contact with the acid for some years. This residual substance, after being washed with cold water until free from acid, is completely soluble in hot water, from which it may be precipitated by alcohol in the form of a brilliant white powder, which is highly crystalline in appearance when the precipitation has taken place slowly. This, under the microscope, is seen to consist of sphæro-crystals made up of thin needles or plates arranged radially, and so closely resembling the sphæro-crystals of inulin that the two substances cannot be distinguished by microscopical examination alone. This substance has been termed amylo-dextrin by Naegeli. It gives an intense reddish-brown coloration with iodine (Brown and Morris, Trans. Chem. Soc. 1889, 449).

The further action of acids on starch differs very considerably according to the degree of concentration, temperature, and pressure.

When starch is heated to boiling with very dilute acids (2 p.c.), little or no formation of paste takes place, the starch being rapidly converted first into soluble starch, then into dextrin and maltose, and, if the action be sufficiently prolonged, finally into dextrose. If this action be stopped at various stages by neutralising the acid with calcium or barium hydroxide, and the filtrates examined at a very early period, the liquid will be found to consist almost entirely of a solution of soluble starch. Later on, this disappears, giving rise to dextrin and maltose; and, according to Brown, Morris, and Moritz (Eng. Pat. of 1889, 10093), to a series of intermediate bodies known as maltodextrins. A little later, dextrose makes its appearance, and this continues to increase at the expense of the maltose already formed, the dextrans and maltodextrins being successively hydrolysed to this body, until finally dextrose only is found in solution. If, however, the action be carried to this extreme point, the dextrose in its turn is acted upon by the acid, giving rise to condensation products, caramel, and other humous substances (Valentin, Jour. Soc. Arts, 24, 404; Scheibler and Mittelmeier, Ber. 23, 3060).

At temperatures higher than 100°, or under pressure, the above changes take place very rapidly. Tables VI. and VII. give some idea of these relative changes.

11. *Action of chlorine, bromine, and iodine.*—Chlorine gas is said to have no action on starch granules either in the dry state or when moistened with water, but when passed through thin starch paste for some hours the viscosity disappears, the greater portion of the granulose becoming converted into soluble starch and erythro-dextrin; this action takes place slowly in the cold, but quickly at a high temperature.

Bromine colours starch granules yellow, but does not seem to form any definite compound,

as the yellow colour disappears on repeatedly washing the granules with water.

Very little action is produced on starch paste by bromine in the cold, but if heated on the water-bath for some time the starch paste is liquefied and converted into the soluble form.

TABLE VI.—*Action of sulphuric acid (dilute) on starch at different temperatures.*

Time	Colour of solution	Iodine reaction	$[\alpha]_{D^{38.6}}$	$K_{3.86}$
<i>Series A.—2 p.c. acid. Temperature, 150°C.</i>				
30 secs.	None	Full brown, trace of starch	142.2	42.3
2 mins.	None	Brown	87.2	62.2
5 "	Slight	None	61.7	89.1
10 "	Much	—	56.8	81.2
30 "	—	—	54.3	71.6
<i>Series A.—2 p.c. acid. Temperature, 125°C.</i>				
2 mins.	None	Blue	All soluble starch	
5 "	None	Brownish-violet	163.0	29.2
10 "	None	Brown	128.6	55.4
<i>Series B.—1 p.c. acid. Temperature, 150°C.</i>				
30 secs.	None	Full brown	152.6	32.2
3 mins.	None	None	83.5	59.6
5 "	Light-straw	—	61.1	78.7
<i>Series B.—1 p.c. acid. Temperature, 125°C.</i>				
10 mins.	None	—	153.4	34.3
20 "	None	—	118.5	55.6
30 "	None	—	97.2	69.7

TABLE VII.—*Action of various acids on starch at 150°C.*

Acid	Time	$[\alpha]_{D^{38.6}}$	$K_{3.86}$
0.25 p.c. Sulphuric .	10 mins.	138.9	38.2
0.25 " Hydrochloric	10 "	60.6	84.1
2 p.c. Phosphoric .	10 "	117.8	55.1
1 " Tartaric .	20 "	170.3	24.6
1 " Oxalic .	10 "	94.4	76.5
1 " Acetic .	30 "	No action	

The most characteristic reaction for starch, wherever it occurs, is the production of a deep-blue coloration with a solution of iodine. This coloration is imparted by the iodine to the intact starch granules as well as when in the condition of starch paste and of soluble starch. This iodine reaction was discovered as far back as the year 1813 by Stromeyer, and has been the subject of much investigation since then.

The production of the blue coloration when starch is treated with iodine was formerly generally regarded as due to the formation of a compound of iodine and starch, although Duclaux had given his opinion that it was a physical rather than a chemical phenomenon. In more recent times, F. Mylius (Ber. 1887, 20, 688) ascribed to the supposed iodide of starch the formula $(C_{24}H_{40}O_{20})_4 \cdot HI$, whilst Seiffert (Jahresber. Thier. Chem. 1888, 21) regarded it as $(C_{24}H_{40}O_{20})_6 \cdot I_7$. G. Rouvier (Compt. rend. 1892, 114, 128, 749, 1366; 1893, 117, 281, 461; 1894, 118, 743; 1895, 120, 1179) believed at first that iodide of starch should be represented by the formula $(C_6H_{10}O_5)_4 \cdot I$, whilst in subsequent papers he adduced evidence of the existence of four compounds, viz. $(C_6H_{10}O_5)_{16} \cdot I_2$;

$(C_6H_{10}O_5)_{16}I_3$; and $(C_6H_{10}O_5)_{16}I_4$. Finally (*ibid.* 1897, 124, 565) Rouvier suggested that the power of the lower iodide to dissolve a further quantity of iodine in the supernatant liquid was in accordance with the law of Berthelot and Jungfleisch concerning the partition of two non-miscible solvents. Syniewski deduces the formula of the iodide from his experiments, making use of his formaldehyde amyloextrin $[(C_{54}H_{90}O_{45} + 1\frac{1}{2}H_2O)I_3]_4$, which corresponds with 20.5 p.c. of iodine. He suggests that the iodine probably attaches itself to the terminal CH_2OH groups (*see* The Constitution of Starch, v. Syniewski, *Annalen*, 1902, 324, 212–268). F. W. Küster (*Annalen*, 1894, 283, 360; *Ber.* 1895, 28, 783) came to the conclusion that the so-called iodide of starch is neither a compound nor a mixture but a solution of iodine in starch. Similar views are held by A. Meyer (*l.c.*). This view appears to be the most probable, and the colorations produced by iodine with the starches and dextrans may perhaps be regarded as iodine sols., the factor which determines the colour being the molecular complexity of the colloidal carbohydrate.

The coloration of starch and iodine is discharged when an aqueous liquid exhibiting it is heated; it returns, however, on cooling, unless the liquid has been boiled for a protracted period. In the latter case the iodine may have been converted into hydrogen iodide or may have been volatilised. It is also discharged when treated with alcohol, alkalis, arsenious acid, or sodium hydrosulphite. H. B. Stocks (*Chem. News*, 1887, 56, 212; 1888, 57, 183) stated that when silver nitrate is added to iodide of starch it is decolorised, silver iodide and iodate being formed.

According to v. Euler and Myrback (*Arkiv. Kem. Min. Geol.* 1922, 8, No. 9, 1; *Chem. Soc. Abstracts*, 1922, i. 1120) there is evidence for the existence of two compounds of iodine and potato starch, to which the formulae $(C_6H_{10}O_5)_{18}I_2$ and $(C_6H_{10}O_5)_{18}I_4$ are given. Soluble starch has less affinity for iodine than potato starch. Hydrogen iodide does not appear to be necessary for the formation of the blue colour.

A. Lottermoser, dealing with the constitution of iodide of starch (*Zeitsch. angew. Chem.* 1921, 427; *see* Chemical Society's Abstracts, 1921, 708), concludes from the results of electric potential and other physical measurements, that the supposition of Biltz and others that the so-called iodide of starch is an adsorption compound of starch and molecular iodine is justified. Neither iodion nor potassium iodide is adsorbed by starch to any appreciable extent, but experiments indicated that in *N*/100 or less potassium iodide solutions there is a noticeable adsorption of tri-iodion. In *N*/10- or *N*/5-solutions this is, however, so small as to be negligible. In general, the results confirmed the statement of Mylius, that for the formation of the blue colour the presence of iodion is necessary, since it participates, if only very temporarily, in the adsorption.

L. Berczeller (*Biochem. Zeitsch.* 1922) also considers iodide of starch to be an adsorption compound. Less iodine is taken up from alcohol than from water, and none from benzene or carbon tetrachloride, and this agrees with experimental results obtained with adsorbent

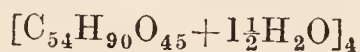
charcoal. Measurements made of the adsorption of iodine by starch solution, by determination of the partition coefficient (between the starch solution and tetrachloroethane), or by dialysis, show that less is adsorbed than with solid starch.

The partition of iodine between starch, aqueous potassium iodide, and carbon tetrachloride was determined by A. Lottermoser (*Zeitsch. angew. Chem.* 1924, 37, 84), using the partition coefficient of iodine between carbon tetrachloride and *N*/10-potassium iodide (=1.16 at 25°). The partition of iodine between carbon tetrachloride, aqueous potassium iodide, and soluble starch was also examined by the potentiometer method (*cf.* *Chem. Soc. Abstr.* 1922, 1, 10). The results agreed with those obtained by ultra-filtration of the starch iodide solution and analytical determination of the individual components before filtration and in the ultra-filtrate. Starch iodide is thus shown to be an adsorption product. The I_3 -ion is most strongly adsorbed, the adsorption curve being normal. At the same time, the I -ion and undissociated KI and KI_3 are also adsorbed, whilst the expulsion of free iodine from the surface generally increases with increasing concentration. The determination of the partition of iodine between benzene, water, and starch (*cf.* v. Euler and Myrback, *A.* 1922, i. 527, 1120) gave unsatisfactory results owing to the uncertainty of the partition coefficient of iodine between benzene and water. Analogous experiments using carbon tetrachloride in place of benzene give results in agreement with those quoted above, so that there is no evidence of chemical combination between the iodine and starch. Adsorbed iodine is given up again very incompletely by starch, so that the curves obtained by adjusting the equilibrium from 'above' and 'below' do not coincide. The actual adsorption equilibrium is, however, rapidly attained, but the starch continues to adsorb iodine owing, apparently, to a very gradual diffusion of the latter into it (*Chem. Soc. Abstr.* 1924, 126, i. 373).

12. *Action of other reagents.*—Potassium permanganate exercises a powerful oxidising action on starch, but instead of dextrin a series of gummy acids are produced, which reduce Fehling's solution only to a very slight extent. Powdered potassium permanganate is added to a 2½ p.c. starch paste; much carbonic acid is evolved, and manganese dioxide precipitated. The solution is filtered, neutralised with acetic acid, concentrated lead acetate solution added, the resulting precipitate washed with hot water, decomposed with hydrogen sulphide, the solution concentrated and poured into absolute alcohol, when a curdy precipitate is formed. This is washed with absolute alcohol and ether, and dried *in vacuo* over sulphuric acid. The bodies formed possess dextro-rotatory powers, which vary according to the quantity of permanganate employed, and give reactions with iodine from reddish-violet, through reddish-brown, to brown. The elementary analysis of a product which was not coloured by iodine agreed with the formula $C_{12}H_{22}O_{11}$, $C_{12}H_{20}O_{10}$ (Lintner, *Zeitsch. angew. Chem.* 1890, 546).

Formaldehyde causes the starch granules to swell gradually to a thick jelly, which ceases to give a coloration with iodine, becoming

limpid after several days, and capable of filtration after a few months. This filtrate, when allowed to evaporate spontaneously, solidifies to a crystalline mass, which is a compound of starch and formaldehyde and polymerised formaldehyde. When warmed both free and combined formaldehyde volatilise, leaving a substance which gives a blue colour with iodine, and which, on analysis, yields values agreeing with the formula



and which Syniewski considers to be identical with his amyloextrin. The action of formaldehyde in a concentrated solution of starch is considered to be a carbinol hydrolysis, the product 'formaldehyde amyloextrin' being hydrolysed with extreme ease (*v. Syniewski, Annalen, 1902, 324, 201*).

When chloroform is added to a solution of starch in zinc chloride and allowed to remain three months the whole of the starch is converted into dextrin.

When starch paste is treated with chloroform a soluble modification of starch similar to that obtained by the action of hydrochloric acid is formed, and on heating a mixture after some months the starch dissolves and separates as a fine paste on cooling.

When 1 part of starch is shaken with 100 parts of a solution of chloral hydrate (10 parts water to 7 parts chloral hydrate) an almost clear viscous solution is obtained, which does not give a blue coloration with solid iodine or a solution of iodine in chloral hydrate.

Tannic acid gives a flocculent leathery precipitate with starch paste, as well as with soluble starch, which is soluble in boiling water but is reprecipitated on cooling.

13. *Action of enzymes.*—Certain enzymes exert a most powerful action on gelatinised starch, as well as on some of the varieties of starch in the raw state. Of these, the most active are the diastase of malted barley, the saliva, and the pancreatic juice.

If the action of a solution of any one of these enzymes on starch paste be studied, the first effect produced will be complete liquefaction of the paste, and the production, in a short space of time, of a perfectly limpid liquid. At this instant, if the liquid be tested with iodine, a reaction for pure soluble starch may be observed; immediately following this comes the saccharification of the soluble starch. The blue colour produced by iodine disappears, giving place to a reddish-brown colour, indicating the presence of erythroextrin, which in turn becomes transformed into achroodextrin, when iodine ceases to impart any longer a colour to the liquid. Concurrently with the disappearing of the starch, the proportion of sugar goes on increasing, and continues to do so for a considerable time after the iodine has ceased to show any reaction.

Although starch in some form or other enters so largely into the food of man and beast, it was not until early in the last century that it received any attention from the hands of chemists. Since that time, however, much attention has been bestowed upon the changes which it undergoes under the influence of heat, acids, and certain vegetable and animal extracts, and

much valuable information has resulted therefrom.

Considering the very important part which starch plays in several industrial processes on the one hand, and how a careful study of its various transformations serves to throw very considerable light upon many questions connected with vegetable, as well as animal, physiology, it will, perhaps, not be altogether out of place to give, as briefly as possible, a history of the transformations of starch from the earliest up to the present time.

14. *History of starch transformations.*—In the year 1811 Vauquelin discovered that when starch is heated to a high temperature it is converted into a substance completely soluble in water, and which resembles gum arabic in many of its physical properties. In the following year Vogel found that a similar substance is formed when starch is acted upon by hot dilute acid. About the same time, Kirchof discovered that starch, when boiled with dilute sulphuric acid, yields a crystallisable sugar; and two years later, in 1814, the same chemist observed that a similar transformation is brought about by the action of the vegetable albumin of grain, and also that the action of this substance is much intensified by subjecting the grain to the malting process.

The gummy substance produced from starch by the action of dilute acid was first carefully examined in 1833 by Biot and Persoz, who gave to it the name of *dextrin*, from the property which it possesses of rotating a polarised ray of light strongly to the right.

Payen and Persoz observed that dextrin is formed from starch by the action of an infusion of malted grain, a change which they attributed to the presence of a particular transforming agent which they named *diastase*, from its supposed property of separating the interior of the starch granules from their outer envelope. They were the first chemists who prepared dextrin from starch by the action of diastase, and describe it as a substance soluble in cold water and in dilute alcohol, and as not coloured by iodine. A few years later Payen stated that the specific rotatory power of his dextrin was equal to that of starch, and that its elementary composition was indicated by the formula $C_6H_{10}O_5$.

In 1860 Musculus brought forward evidence showing that dextrin and sugar are not successively formed products, but are produced simultaneously by a splitting up of the starch molecule.

The dextrin described more in detail by Musculus in 1865 was a body not coloured by iodine, and not reducing Fehling's solution. In 1871 Griessmayer described two of these substances as dextrin I. and dextrin II. respectively. The first was coloured red by iodine, whilst the second gave no coloration. In the following year O'Sullivan distinguished them as α and β dextrin. These are now more generally referred to as erythroextrin and achroodextrin respectively, names first proposed by Brücke in 1872 as indicative of their behaviour with iodine.

In a series of most interesting and important researches extending from 1872 to 1876 (*Trans. Chem. Soc.* 25, 579; 29, 479; 30, 125) C. O'Sullivan proved most satisfactorily that the

sugar produced by the action of diastase or acid on starch is not, as had up to this time been generally supposed, dextrose, but a disaccharide having a considerably higher specific rotatory power than dextrose, and a much less reducing action upon Fehling's solution.

This body had been previously isolated, as far back as the year 1819, by De Saussure, who, however, merely described its crystalline appearance. It was prepared in 1847 by Dubrunfaut, who, from its optical properties, recognised it as a distinct sugar and named it *maltose*. His observations, however, obtained but little notice at the time of their publication, and appear to have been entirely forgotten until the re-discovery of maltose by O'Sullivan in 1872 (Trans. Chem. Soc. 25, 579). This investigator also gave the results of his examination of the dextrins prepared by the action of diastase and of acid on starch. These results led him to the conclusion that the dextrins from both sources possess the same specific rotatory power of $[\alpha]_D = +213^\circ$, and have an elementary composition corresponding to the formula $C_6H_{10}O_5$, and although he did not succeed in obtaining any of the dextrins absolutely free from a reducing action on Fehling's solution, yet he adduced good evidence to show that in a state of purity they would possess no reducing action. Both these dextrins were said to be slowly converted into maltose by the action of diastase.

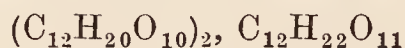
O'Sullivan's work was of great importance in indicating the restricting effect of raising the temperature on the hydrolysis of starch in presence of diastase. It was followed by that of Brown and Heron in 1879 (Trans. Chem. Soc. 35, 596), who confirmed, to a large extent, O'Sullivan's results.

As the result of their experiments Brown and Heron were led to adopt the formula $10(C_{12}H_{20}O_{10})$ for soluble starch.

In 1879 Herzfeld (Ber. 12, 2120) found that in addition to maltose and dextrin a third substance, maltodextrin, was under certain circumstances formed by the action of diastase on starch paste. This compound was regarded by him as being intermediate between achroodextrin and maltose; it was insoluble in alcohol of 90 p.c., and completely fermentable by yeast, possessing a specific rotatory power $[\alpha]_D = 171.6$, $K = 23.5$. It was further investigated by Brown and Morris (Trans. Chem. Soc. 1885, 47, 527). They found that when the action of malt extract on starch paste is limited there always occurs amongst the products of transformation, besides maltose and dextrin, a third substance which is more soluble in alcohol than the dextrins, and has a specific rotatory power of $[\alpha]_{D^{38.6}} = 193.1$ and a cupric reducing power of $K_{38.6} = 21.1$, corresponding to an apparent composition of 34.6 p.c. maltose and 65.4 p.c. dextrin. It is completely hydrolysed to maltose by the action of malt extract at 50° – 60° .

Maltodextrin is not fermentable by yeast (*S. Cerevisia* of the high fermentation), but is slowly hydrolysed into maltose and thus rendered fermentable by certain forms of saccharomyces of the secondary fermentation (*S. Pastorianus*, *S. ellipsoideus*). Brown and Morris considered that maltodextrin was not, as supposed by Herzfeld, a mere hydrolysis product of achroodextrin,

but was produced from starch and the polymeric dextrins by the fixation of a molecule of water upon the ternary group $(C_{12}H_{20}O_{10})_3$, of which there could not be less than five in the starch molecule, which resulted in the separation from the dextrin residue of maltodextrin

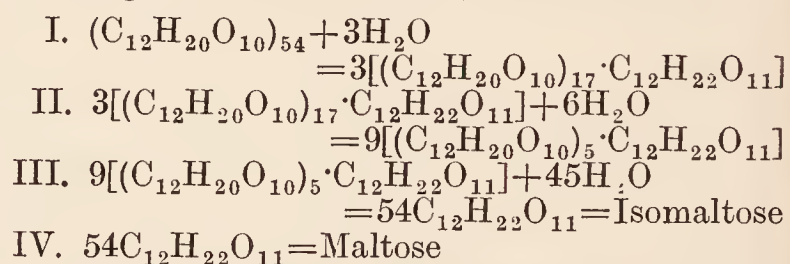


This by the fixation of two more molecules of water gave rise to freely fermentable and crystallisable maltose.

Further experiments in connection with this subject have induced Brown and Morris to alter their views with regard to the dextrins (Trans. Chem. Soc. 1888, 53, 610; 1889, 55, 450, 462; Trans. Lab. Club. 3, 81), which they consider are, after all, not polymeric but metameric.

In 1891 C. J. Lintner (Zeit. ges. Brau. 1891, 284) claimed to have separated from a burr residue by means of phenylhydrazine an osazone readily soluble in hot water, and melting at 152° – 153° , which he called *isomaltosazone*.

Subsequently Lintner and Düll found that after the maltose had been removed from the products of starch conversion by fermentation, they were able by repeated precipitation with alcohol to resolve the unfermented matters into dextrin and *isomaltose*, no trace of an intermediary dextrin being found. They describe *isomaltose* as an intensely sweet-tasting body having an optical rotatory power in a 10 p.c. solution $[\alpha]_D = +139^\circ$ – 140° and $R = 80.0$. Their hypothesis of starch, transformed with diastase, starting from soluble starch, is as follows:—



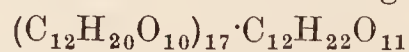
They considered that this action proceeded irregularly, some of the soluble starch molecules being broken down much more rapidly than others, the presence of maltose and the higher dextrins in high-angled transformations being explained by this means.

In 1892 Schifferer, working on the same lines as Lintner, practically confirmed his views with regard to *isomaltose*.

In 1893 Lintner and Düll described the properties of several bodies which they had isolated from the products of starch transformation after long and tedious fractionation with alcohol of different strengths. These were as follows:—

Amylodextrin.—A loose white powder slightly soluble in cold water, readily soluble in hot water. $[\alpha]_D = +196$, does not reduce Fehling's solution, gives a deep coloration with iodine, and is the principal constituent of soluble starch. The formula is given as $(C_{12}H_{20}O_{10})_{54}$.

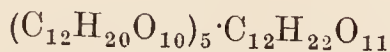
Erythro-dextrin.—This body is readily soluble in water $[\alpha]_D = +196$, reducing power, $R = 1$ (= 1 p.c. that of maltose), and gives a reddish-brown colour with iodine. The formula given is



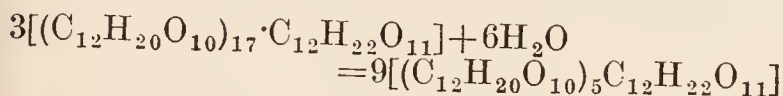
and it is formed from amylo-dextrin as follows:



Achroodextrin I.—This dextrin is soluble in water; $[\alpha]_D + 192$, reducing power R 10, and gives no coloration with iodine. The formula given is



and it is formed from erythro-dextrin as follows :



Achroodextrin II.—Only found in very small quantities in transformation products by the action of diastase $[\alpha]_D = +180$, reducing power R 24.

In 1895 Ost (Chem. Zeit. 1895, 1501) investigated the dextrins in a starch transformation, and isolated a dextrin having a rotatory power $[\alpha]_D = +180^\circ - 183^\circ$, and reducing power R 28-33, and gave as its formula $C_{36}H_{62}O_{31}$. This he believed to be identical with Lintner and Düll's achroodextrin II., and to be contained in Brown and Morris' maltodextrin $[\alpha]_{D_{3.86}} + 171^\circ$, R 34. He made the observation that it was improbable that dextrins of absolute purity could be prepared, as it is extremely probable that they may undergo some little change during the process of isolation.

In 1895 Ling and Baker (Trans. Chem. Soc. 1895, 43, 702) published the results of their investigations on the isomaltose discovered by Lintner, which threw much doubt on the existence of this compound.

Working with diastase prepared from air-dried malt on the same lines as Lintner and Düll, they obtained a substance having a sweet but by no means intensely sweet taste, with an optical rotatory power of $[\alpha]_{D_{3.86}} + 144.5^\circ$, and R 79.6. It yielded an osazone having a m.p. between 160° and 170° , and the results of its ultimate analysis and its molecular weight gave figures which indicated a disaccharide. When submitted to the action of diastase it showed an optical rotatory power of $[\alpha]_{D_{3.86}} + 131.2^\circ$, and R=94.5, these changes not being accompanied by any change in the specific gravity of the solution. When acetylated by Liebermann's method, the substance gave nearly half its weight of ocacetylmaltose. They concluded that Lintner's 'isomaltose' was a mixture of maltose and a simple dextrin, having the formula $C_{12}H_{20}O_{10} + H_3O$.

When working with diastase obtained from high-dried malt they obtained a substance yielding an osazone having a melting-point identical with Lintner's isomaltosazone, which on analysis proved to be an osazone of a hexatriose. They also found a certain amount of glucose was produced in transformations with diastase obtained from kiln-dried malts (cf. p. 358).

In a later paper, Ling and Baker (Trans. Chem. Soc. 1895, 43, 739) showed that the osazone obtained from the so-called isomaltose could be fractionated by recrystallisation into portions having melting-points corresponding to maltosazone and a substance which analysis indicated to be a disaccharide, and which they regarded as impure maltosazone. The presence of glucose was always detected in starch transformations with diastase from kiln-dried malt, but the osazones from the transfor-

mation products soluble in 90 p.c. alcohol were characteristic of Lintner's isomaltose, and gave analytical results between those required for the osazone of a disaccharide and that of a trisaccharide. It thus appeared as if a trisaccharide was a product of the action of diastase from kiln-dried malt. As an explanation of this they suggest that the trisaccharide might be formed by the condensation of a molecule of a simple dextrin with one of glucose under the influence of phenylhydrazine.

Brown and Morris (Trans. Chem. Soc. 1895, 43, 702) published results of their investigations which also threw doubt on the existence of isomaltose. They first pointed out that it does not conform to their 'law of definite relation.' This law was the outcome of H. T. Brown's work in conjunction with others up to this date, and was as follows: The composition of the mixed products of a starch transformation by diastase or of any fractionated portions of such products can always be consistently interpreted in terms of maltose, having an optical activity of $[\alpha]_D + 138^\circ$, and a reducing power of R 100, and a non-reducing dextrin having an optical activity of $[\alpha]_D + 202^\circ$.

Lintner's isomaltose was said to possess an optical activity equivalent to $[\alpha]_j + 156^\circ$ and K 48.8. According to the law this optical rotatory power requires a reducing power of K 55.3; and a reducing power of K 48.8 requires an optical rotatory power of $[\alpha]_j + 163.2$. They came to the conclusion that isomaltose could be split up by fractionation, fermentation, &c., in such a manner as to indicate that it was a mixture of the amyloin type.

A study of the osazone led them to the belief that it was maltosazone modified in its crystalline structure and melting-point by the presence of an impurity, and they were able to compel maltosazone to crystallise in the isomaltose form by the addition of a trace of an amorphous product of the reaction. They found that 50-60 p.c. of isomaltose was fermentable, and their investigations led them to believe that the matter fermented was maltose, and that the unfermented portion approached very closely in composition that of an amyloin containing two amyloin groups and one amylin group.

In the same year Ost (Chem. Zeit. 1895, 1501), following the instructions of Lintner and Düll, made an attempt to isolate isomaltose. He found that their methods were not satisfactory, and after removing the maltose from the alcoholic extracts by means of crystallisation, he obtained osazones from the residue similar to those said to be characteristic of isomaltose, but which on further investigation proved to be maltosazone. He confirmed Brown and Morris's and Ling and Baker's views, that mixtures of maltose and dextrin, when heated together, produced an osazone simulating isomaltosazone. No osazone was obtained in starch transformations where the whole of the maltose had been removed by fermentation, and from those in which a portion of the maltose had been left unfermented he obtained osazones similar to isomaltosazone. Ost's conclusions agreed with those of Ling and Baker, and Brown and Morris in that isomaltose has no

real existence, and that the *isomaltosazone* of Lintner and Düll is modified maltosazone.

He came to the conclusion, after an investigation into the products of starch transformation by diastase, that starch itself has the composition $(C_{12}H_{20}O_{10})_n$, n indicating a large but unknown number. He freely criticises the results and theories put forward by previous workers, holding the non-reducing dextrin of Brown and Morris to be non-existent, and that their law of 'definite proportion' is not always fulfilled even in their own experiments, and is certainly not in the achroodextrin II. which he had prepared. He considers that the theory of Brown and Heron should have been entirely abandoned instead of being altered to the amyloin theory after maltodextrin and amylo-dextrin had been recognised as individual substances. He threw doubt on the molecular weight determinations, especially those of the higher dextrans, and regarded erythro-dextrin as a mixture of starch and achroodextrin.

Mittelmeier (Zeitsch. angew. Chem. 1895, 552) put forward a theory based on his investigations that the starch molecule under the action of diastase is split up into two amylo-dextrans, which he terms primary and secondary erythro-dextrin. The primary erythro-dextrin is rapidly converted into maltose in the time that the secondary reached the stage in which it gives a red coloration with iodine, in this way he explains the presence of the highest dextrans and maltose in the same starch conversions. The optical rotatory power of these erythro-dextrans is about $[\alpha]_D + 170^\circ$; they both reduce Fehling's solution and form osazones. Under the influence of diastase primary and secondary achroodextrans are obtained.

In 1897 Ling and Baker (Trans. Chem. Soc. 1897, 71, 509) gave some further results of an examination of the products of the limited action of diastase on potato starch paste at 70° . They obtained the following compounds, the composition and molecular weight of which they established by ultimate analysis and cryoscopic determinations.

Maltodextrin- α $C_{36}H_{62}O_{31}$ (identical with the maltodextrin of Brown and Morris) having optical and reducing powers of $[\alpha]_D + 180^\circ$; R 32.8.

Maltodextrin- β $C_{24}H_{42}O_{21}$ (identical with a body isolated by Prior in 1896 (Bayr. Brau. J. 1896, 157), which he termed achroodextrin III.) having the constants $[\alpha]_D + 171.6^\circ$; R 43.

From the fraction designated *isomaltose* by Lintner an unfermentable substance was obtained, having the constants $[\alpha]_D + 156^\circ$; R 62.5, which probably consists principally of a substance having the formula $C_{12}H_{20}O_{10} + H_2O$. Later work by Ling (J. Inst. Brewing, 1911, 579) has shown the probable existence among starch conversion products (obtained by the action of diastase on starch paste), besides the higher dextrans of the following compounds:

Maltodextrin- α $C_{36}H_{62}O_{31}$.

Maltodextrin- β (achroodextrin III.), $C_{24}H_{42}O_{21}$.

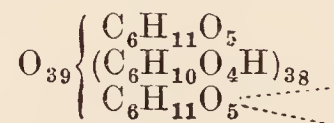
Maltose $C_{12}H_{22}O_{11}$.

Dextrinose or Isomaltose $C_{12}H_{20}O_{10} + H_2O$
(see Syniewsky, p. 336).

Dextrose $C_{6-12}H_{10-20}O_6$.

In 1898-1899 Brown and Millar (Trans. Chem.

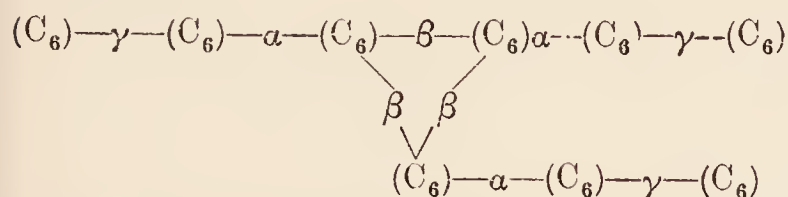
Soc. 1899, 75, 286-337) tried to isolate the intermediate products of saccharification by conversion into nitric acid esters. Owing to oxidation, however, this was unsuccessful; but by moderate oxidising agents dextrinic acids were obtained. Starting with the maltodextrin of Brown and Morris they first obtained an acid which they termed 'maltodextrinic acid A.' This can be hydrolysed in two successive steps, by diastase and acids respectively, into first an acid which they term maltodextrinic acid-B, together with maltose, and, secondly, into a pentose acid and glucose. In further experiments they obtained a dextrin with optical and reducing properties corresponding to $[\alpha]_D 195^\circ - 195.7^\circ$; R 5.7-5.9, which they claim is a stable dextrin, proving this statement by the products of oxidation. On the data furnished by their researches they base their theory that the dextrin molecule may be empirically regarded as made up of $39C_6H_{10}O_5$ groups in combination with a terminal $C_6H_{12}O_6$ group; or in other words, a condensation of fatty glucose molecules with the elimination of $39H_2O$, the constitutional formula being—



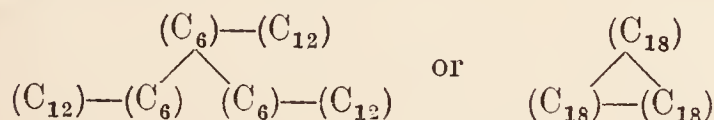
In 1900 and 1902 V. Syniewski (Annalen, 1900, 309, 282; 1902, 324, 212) brought forward a new theory on the breaking down of the starch molecule by hydrolysis. He points out that starch can be hydrolysed in two ways, either so as to yield substances which do not reduce alkaline copper solutions (carbinol hydrolysis), or those which do reduce alkaline copper solutions (carbonyl hydrolysis). The simplest product of the carbinol hydrolysis of starch is a substance amylogen $C_{54}H_{96}O_{48}$, which is obtained by the action of sodium peroxide on potato starch. He finds that by heating starch paste at 140° in an autoclave carbinol hydrolysis occurs and proceeds as far as amylo-dextrin $C_{216}H_{372}O_{186}$. By treating this amylo-dextrin with malt extract previously heated at 78° for 18 minutes the solution contained exclusively a product identical with the maltodextrin of Brown and Morris, the achroodextrin II. of Lintner and Düll, and the maltodextrin- α of Ling and Baker, and which he denotes limit dextrin II. Elementary analysis and determination of the molecular weight established the formula $C_{36}H_{62}O_{31}$, having constants $[\alpha]_D 179.36^\circ$; R 30. Further hydrolysis of this product with malt extract to a point where the reducing power of the dissolved bodies was R 50 gave a product consisting mainly of a compound $C_{24}H_{42}O_{21}$, which was identical with Prior's achroodextrin III., and Ling and Baker's maltodextrin- β , which he called γ -maltodextrin, having constants $[\alpha]_D 172.17^\circ$; R 42.7. Both limit dextrin II. and γ -maltodextrin on complete hydrolysis with malt extract yield a mixture of maltose and *isomaltose* or, as the author terms it, dextrinose $C_{12}H_{22}O_{11}$, with constants $[\alpha]_D 141.4^\circ$; R 84.5.

Syniewski considers the theories of Lintner and Düll and of Brown and Morris on the mechanism of starch hydrolysis to be untenable, and elaborates a theory of his own. He regards

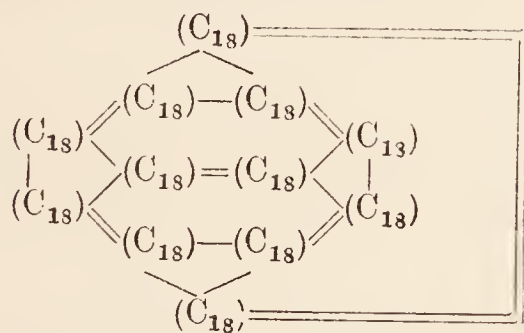
the starch molecule as made up of amylogen residues, and he assumes that the nine glucose groups which make up the amylogen residue $C_{54}H_{90}O_{45}$ in the starch molecule are connected together by nine carbonyl bonds of three different kinds which he denotes as α -, β -, and γ -bonds. The amylogen residue may be thus represented—



The three monocarbonyl bonds which unite three maltose residues with the residue of limit dextrin I. are α -bonds. The three monocarbonyl bonds which are between the three glucose groups of the limit dextrin I. residue are β -bonds, and those bonds which unite the glucose groups of the maltose residues are γ -bonds. The amylogen residue may also be represented as follows:—



The composition of starch is represented by the formula $[(C_{54}H_{96}O_{48})_n - 3H_2O]$, whilst that of amylopectin is represented by the formula $n[C_{54}H_{90}O_{45} + 1\frac{1}{2}H_2O]$. By the action of malt extract heated to 78° amylopectin may be completely converted into limit dextrin II. $C_{36}H_{62}O_{31}$. From this it follows that n must be a whole number. Limit dextrin II. is formed from two different amylogen residues, and this conclusion is arrived at from the assumption that the β -carbonyl bonds are disrupted in its formation. From certain geometrical considerations the value of n in the potato starch molecule is considered to be 4, its empirical formula being $C_{216}H_{360}O_{180}$, which is thus graphically represented—



According to this formula each amylogen residue in the starch molecule is united by six carbinol anhydride bonds, three of these being between limit dextrin I. residue and three between maltose residues. The former are denoted d -bonds, the latter m -bonds. The single lines between the C_{22} -groups forming a dextrin ring are β -carbinol bonds; the double lines uniting two C_{18} -groups are carbinol bonds, one being a d -bond and the other an m -bond. It is conceivable that the molecular constitutions of other starches are analogous but contain a different number of amylogen residues, thus 2, 8, or 20. The author goes on to explain the several steps in the process of hydrolysis of the starch molecule, for which the reader is referred to the original papers or extracts of this in Jour. Inst. Brew. 1900, 6, 110; and 1902, 8, 732-737.

There is no doubt that much of the obscurity and confusion which has arisen in the interpretation of results up to this period has its origin in the fact that starch has been too generally regarded as a chemically uniform substance. From about this time onward most of the work on starch has been directed to the investigation of the nature and structure of the starch granule, and also to a closer study of the transforming enzyme *diastase*.

Potter (Annales de l'Institut. Pasteur, 1899, 665, 728, and 796) was among the first to work on these lines. He found two distinct phases in the saccharification of starch paste, one of extraordinary rapidity, and the other increasingly sluggish, and from among the possible causes of retardation he dismisses the weakening of the enzyme and the inhibitive effect of the soluble products, forming the conclusion that since the slackening refers to the production of dextrins as well as maltose, the lack of uniformity must exist in the starch itself.

In 1902 Ling and Davis (J. Inst. Brewing, 1902, 8, 475) showed that the unrestrained action of diastase at the temperature at which its activity is at its optimum, namely 55° , carried the transformation of starch paste to a point at which the constants of the substances in solution were substantially those of maltose. They formed the opinion that the so-called No. 8 equation of Brown and Heron is not really a resting stage in the reaction, but only marks a slowing down, the reaction continuing at a reduced rate until the end. When the diastase is heated in solution above 60° its action weakened and an alteration is produced in the enzyme molecule, this alteration being assumed by the production of d -glucose when it acts on starch paste. The amount of d -glucose formed depends on the temperature at which the diastase in solution is heated before adding to the starch paste, the maximum amount being obtained when the solution has been previously heated at 68° - 70° for about 20 minutes. The amount of d -glucose formed in any case does not exceed about 12 p.c. of the total hydrolytic products.

In 1903 Brown and Millar showed that the so-called stable dextrin, one of the products of hydrolysis of starch by diastase, is converted by the further action of diastase into about equal parts of d -glucose and maltose.

Ling (Brit. Ass. Rep. 1903; J. Fed. Inst. Brewing, 1903, 9, 446) confirmed the statement of Brown and Millar, and found further that other products of diastatic action with the exception of maltose, yield a proportion of d -glucose when submitted to the further action of diastase; thus maltodextrin- α of Ling and Baker, when treated in 3 p.c. solution with an active preparation of diastase at 55° for 140 hours, gave the constants $[\alpha]_{D^{20}} + 127.6^\circ$, $R_{3.93} = 105.6$, corresponding approximately with maltose 90 p.c. and d -glucose 10 p.c. A determination of d -glucose as phenylosazone gave 10.5 p.c. Ling and Rendle (Analyst, 1904, 29, 243) find that commercial concentrated malt extracts invariably contain d -glucose, and they believe that the latter is produced during the evaporation of the extract by the action of the

diastase on the products of the partial hydrolysis of starch.

In 1904, following on these results, came the new theories brought forward by Maquenne and Roux on the structure of the starch granule, and the discovery by Fernbach and Wolff of the enzyme termed amylocoagulase. These workers formed the opinion that when starch is acted on by diastase the maltose is produced from that portion of the starch granule they termed amylose, and that the residual unsaccharifiable dextrin comes from the amylopectin. A comparison of the action of malt extract at 50° on starch paste and a solution of pure amylose, gave results as follows:—

	Percentage of maltose on original starch substances	
	Starch paste	Amylose
5 minutes	. 66.7 p.c.	94.4 p.c.
1 hour .	. 79.0 „	99.7 „
2 hours .	. 81.1 „	100.1 „
3 „ .	. 82.0 „	101.4 „
28 „ .	. 91.8 „	104.2 „

The apparent halt in the reaction in the case of starch paste when about 80 p.c. of maltose is formed is explained on the assumption that the hydrolysis of the amylose is then complete.

In 1906 Roux (*Compt. rend.* 1906, 142, 95), after further experiments with starch pastes of other starches, prepared at 100°, came to the conclusion that they were similar to potato starch in being composed of amylose and amylopectin. He found that they all tended to give the same dextrin and maltose proportions when acted upon with diastase.

In the same year, Roux, in conjunction with Maquenne (*Compt. rend.* 1906, 142, 124), found that when the alkalinity of starch paste was made exactly neutral to methyl orange with decinormal sulphuric acid, and the malt extract neutralised to the extent of one-third or two-fifths, saccharification proceeded more rapidly, and the yield of maltose showed a large increase.

Fernbach pointed out that malt extract is acid to phenolphthalein and alkaline to methyl orange, as if it contained a mixture of primary and secondary alkali phosphates, the optimum reaction for saccharification being neutrality to methyl orange.

In conjunction with Wolff, Fernbach showed that natural starches were similar in this respect to malt extract, and they found that if starch paste and malt extract be rendered exactly neutral to methyl orange, practically the whole of the starch is converted into maltose by the malt extract.

They came to the conclusion that the transformation of starch by diastase, if allowed sufficient time, will attain the theoretical limit of maltose production, and that the slackening observed in the later stages is due to the dilution of hydrolysable matter, and not to failure of the diastase. Solutions of the residual dextrins separated from an advanced transformation were found to be still susceptible to diastatic action.

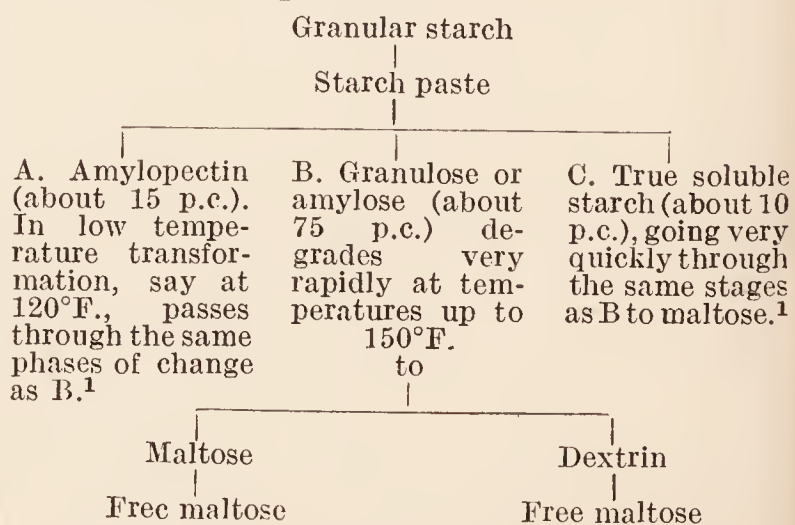
Maquenne and Roux (*Compt. rend.* 1906) practically uphold these observations regarding saccharification, but consider that the reaction has two distinct phases, the first one of extreme rapidity, corresponding to the conversion of

70–80 p.c. of the starch into maltose, the second, a very slow one extending over several days.

In 1907 Van Lear (*Bull. Soc. chim.* 1907, 21, 8) discussed the later work on starch transformation and accepted Maquenne and Roux's amylose and amylopectin hypothesis, but did not agree that the earlier work had been controverted, but rather had been extended. In starch conversions carried on at temperatures below 60°, the amylose may be regarded as being converted very rapidly into maltose with the production of dextrins, the stable dextrin remaining being derived from the amylopectin. At temperatures above 60° dextrins are produced from the amylose of quite a different type, which are easily saccharifiable by malt diastase and correspond with the maltodextrin of Brown and Morris.

We must conclude, therefore, that from starch transformation with malt extract carried on at high temperatures we obtain mixtures of both kinds of dextrins, the complexity of which the older investigators ascribed to the modification of the action of diastase by heat, but which the more recent investigators attribute to the heterogeneous nature of the starch granule itself.

In 1911 Matthews and Lott (*J. Inst. Brewing*, 1911, 17, 219–266), as the result of a long series of experiments, practically endorse the views expressed by Maquenne in 1908 (*see p.* 346) on the structure of the starch granule, but find that experiments with potato starch do not exactly represent what happens with barley and malt starch when acted upon with diastase, but the relationship as to kind of products holds. Discussing dextrin they question whether really stable dextrin exists. Any so-called stable dextrin has its origin in the amylopectin, the part of the starch which requires liquefaction before transformation, any delay or injury to this action resulting in the production of very difficultly degradable dextrin. The weight of evidence appears to be entirely against the maltodextrin theory, but the proportions of combined maltose and dextrin in bodies of this character found in starch transformations mark them as ordinary products of change and representative of an intermediate state. The theory is that there is a stage in starch transformation where the whole of the readily transformable matter is present as a body degradable by successive stages to maltose. The change is represented as follows:—



Most of the work mentioned above has been carried out with carefully purified potato starch,

¹ There is some evidence that a little dextrose may sometimes be formed.

but it has been ascertained that similar experiments made with widely differing starches—such as maize, rice, wheat, arrowroot, sago, barley, and various other starches—practically yield the same analytical results when acted upon in the form of paste by diastase, but it has been found that the same starches differ materially from one another when the unbroken granules are acted upon in the cold, as will be seen from Table VIII. by Lintner (Brauer und Malzkalendar, 1890, 83).¹

Ling (J. Inst. Brewing, 1911, 570) carried out some experiments in which wheat starch, which has since been found to behave similarly towards malt diastase to barley starch (*see* p. 393), was suspended in water and submitted to the action of diastase from malts of varying diastatic power at different temperatures. The malts used were (1) a brewing malt one year old which had originally a diastatic power of 30° Lintner but which (although kept in a closed bottle) had diminished in activity to 23° Lintner

TABLE VIII.—*Action of Diastase on Ungelatinised Starch.*

Starch from	Percentage dissolved by 4 hours' contact at the under-mentioned temperature				Gelatinisation temps.
	122°F.	131°F.	140°F.	149°F.	
Potato starch	0·13	5·03	52·67	90·34	°F. 149
Rice „	6·58	9·68	19·68	31·14	158–167
Barley „	12·13	53·30	92·81	96·24	176
Green malt „	29·70	58·56	92·13	96·26	185
Cured „ „	13·07	56·02	91·07	93·62	176
Wheat „	—	62·23	91·08	94·58	167–176
Maize „	2·70	—	18·50	54·60	158–167
Rye „	25·2	—	93·70	94·50	176
Oat „	9·40	48·50	92·50	93·40	185

at the time of use; (2) a new brewing malt of diastatic power 31° Lintner; and (3) a distillery (Odessa) malt of diastatic power 123° Lintner. The results are explained in the following tables:—

CONVERSION TEMPERATURE 130°F.

D.P. of malt used	Time in hours	P.c. of starch dissolved	Maltose apparent	—
23	1	75	—	—
„	2	79	—	—
„	3	79	—	—
„	4	82	—	—
„	5	85	84	149·2
31	1	—	—	156
„	2	—	—	153
„	3	—	—	151
„	4	—	81	151
123	1	88	68	—
„	2	92	73	152
„	3	95	79	—
„	4	98	83	—
„	5	99	85	—
„	6	100	92	145

¹ See also Die Stärkeumbildenen Fermente Baranetzky 1878, and Brown and Morris, Trans. Chem. Soc. 57, 510.

CONVERSION TEMPERATURE 140°F.

D.P. of malt used	Time in hours	P.c. of starch dissolved	Maltose apparent	—
23	1	94	74	157
„	2	97	74	154
„	3	97	75	154
31	1	100	78	153
„	2	100	79	153
123	1	100	81	148
„	2	100	81	148
„	3	100	81	148

CONVERSION TEMPERATURE 150°F.

D.P. of malt used	Time in hours	P.c. of starch dissolved	Maltose apparent	—
23	$\frac{1}{2}$	95	56	168
„	1	95	59	167
„	2	97	61	166
„	3	97	64	165
„	4	98	64	165
31	$\frac{1}{2}$	95	70	158
„	1	95	70	158
„	1½	95	70	158
123	$\frac{1}{2}$	96	75	161
„	1	96	75	161
„	2	96	75	153
„	3	96	77	151

These results, so far as they are influenced by the diastatic power of the malt used, may be compared with those obtained later from barley and wheat starch as the basis of a method of estimating starch in barley and wheat (*see* curve, p. 393).

The diastase of saliva and of pancreatic extract hydrolyse raw starch and starch paste very similarly to the diastase of malt. Here, however, dextrose is formed at an early stage in addition to maltose and dextrin, the action on raw starches varying according to the kind of starch acted on (*see* Roberts, Digestive Ferments; Church, Food Grains of India; Bell, Chemistry of Foods; Brown and Heron, Proc. Roy. Soc. 1880, 393; Chittenden and Cummins, Chem. News, 51, 256; Chittenden and Smith, *ibid.* 53, 109).

It has been shown by J. L. Baker (Trans. Chem. Soc. 1902, 1177) that when the diastase from ungerminated barley is allowed to act at 50°C. on a solution of soluble starch, hydrolysis proceeds until at the end of an hour to an hour and a half the constants of the dissolved matter are $[\alpha]_{D_{393}}$ 160°–165° and R_{393} 60–65. After this the reaction is a comparatively slow one, and if continued for 96 hours the reducing power is only increased to R_{393} 70, the iodine reaction being still blue.

An examination of the products, after the reaction had proceeded for 1½ to 2 hours, showed

that a dextrin and maltose were the sole products. After 24 hours, evidence of the presence of glucose was obtained, the amount of this sugar apparently increasing in proportion to the time of conversion.

The dextrin, isolated by precipitation with alcohol from the products of the conversion, gave a blue iodine reaction, a specific rotation of $[\alpha]_{D^{20}} 190^{\circ}$ – 195° , and a reducing power of $R_{3.93}$ 0.55–1.0. The alcohol solutions from which the dextrin was precipitated were collected and examined and found to contain maltose, glucose if the conversion period was prolonged, but no trace of any dextrin of less complexity than is described above.

Barley diastase acts on the above-mentioned dextrin very slowly, the constants of the solution after 90 hours at 45° to 50° being $[\alpha]_{D^{20}} 160^{\circ}$ and $R_{3.93}$ 32. The products, which gave a blue iodine reaction, consist of maltose, unaltered dextrin, and glucose. The presence of glucose could be detected in 18 hours, but after 90 hours the amount formed had only slightly increased. The action of malt diastase on this dextrin was more vigorous. After 18 hours at 55°C . the solution, which no longer gave an iodine reaction, had the constants $[\alpha]_{D^{20}} 149.3^{\circ}$ and $R_{3.93}$ 50–51. An examination of the products showed that they consist of maltose, a mixture of achroodextrins, and a considerable quantity of glucose.

Since barley diastase is without action on maltose, the glucose found in the products from the prolonged action of barley diastase on soluble starch must be derived from the dextrin. Barley diastase completely liquefies starch paste in 2 to 3 hours at 50°C ., the products consisting of the above-described dextrin and maltose.

The dextrin obtained by the action of barley diastase on soluble starch or starch paste differs markedly from Nägeli's 'amylodextrin,' which was reinvestigated by Brown and Morris (Trans. Chem. Soc. 1889, 55, 449). In consideration of its general behaviour and close relation to the parent substance starch, the author proposes to term the new dextrin α -amylodextrin (see $\alpha\beta$ -hexa-amylose, p. 361).

Following this work, it was shown by A. Fernbach and J. J. Wolff (Compt. rend. 1907, 145, 80), that when barley extract, which has been kept for 25 days under toluene, is allowed to act on starch paste, previously liquefied by heating at 150°C ., at 30°C . for 332 hours, the most resistant dextrins are converted into maltose though much more slowly than by malt extract. It was found also that the preservation of barley extract caused it to undergo auto-excitation analogous to that observed in the case of malt extract. At the end of 332 hours the starch was almost entirely converted into maltose by the 25-days-old barley extract, whilst the conversion of the starch into maltose during the same period was not complete with fresh barley extract.

15. *Action of bacteria*.—According to Fitz (Ber. 10, 276; 11, 42), starch yields by fermentation with a *Schizomycetes* (*Bacillus butylicus*, *Bacillus subtilis*) 35 p.c. of butyric acid and 9 p.c. of acetic acid, together with a small quantity of succinic acid. Inulin appears to yield the same products.

By the action of certain organisms, starch is

rendered capable of being converted into dextrin and maltose, and eventually into alcohol. In this way the Indians of South America make an alcoholic liquor called *chicha* by the fermentation of the starch of maize. The grain is first allowed to soak for from 4 to 6 hours to soften it and afterwards fermented. The fermentation is due in the first instance to the presence of a minute organism, situated on the epidermis of the grain; this secretes a diastase, which either produces or aids further fermentation (Marcano, Compt. rend. 95, 856).

For the synthesis of starch from sugar by bacteria, see Grey (Bio-Chem. J. 1924, 18, 712; Chem. Soc. Abstr. 1924, 126, i. 912).

Gayon and Dubourg (Compt. rend. 103, 885) mention a species of mucor which has the power of converting dextrin and starch into sugar, and then fermenting the sugar.

Bacillus suavis converts starch gradually into dextrin and glucose, with formation of alcohol, aldehyde, formic, acetic, and butyric acids, &c. (Selavo and Gosio, Arch. ital. Biol. 14).

Villiers (Compt. rend. 112, 435 and 536) finds that the addition of a pure cultivation of *Bacillus amylobacter* to a 5 p.c. starch paste causes complete liquefaction in 24 hours, and on allowing the fermentation to continue some time the liquid no longer gives a blue coloration with iodine, the products of the change being almost exclusively dextrins, no maltose or dextrose being found to be present, from which he concludes that the organism converts starch directly into dextrin without the intervention of any diastase secreted by the ferment.

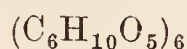
Perdrix (Ann. Inst. Pasteur, 1891, No. 5) has separated from Paris water a bacillus, *B. amylozymicus*, which ferments starch with production of dextrin, glucose, carbon dioxide, ethyl and amyl alcohols, acetic and butyric acids. A somewhat similar change is effected by the bacillus of malignant oedema (Kerry and Fraenkel, Monatsh. 12, 350).

F. Schardinger (Wiener Klin. Wochenschr. 1904, No. 8) announced that he had obtained crystalline dextrins by the action on starch of an organism to which he gave the name *Bacillus macerans*, isolated from a retting vat (see also Centr. Bakt. Par. 1911, [2] 29, 188). *Bacillus macerans* renders potato-starch completely soluble, arrowroot-starch nearly completely so, but has far less effect on rice or wheat starch. Part of the dextrin formed, about 25–30 p.c. of the starch taken, is crystalline, the rest being amorphous and gum-like. Three different crystalline dextrins have been obtained from all four varieties of starch, the yield being under the most favourable conditions 25 p.c. of the starch employed.

The two chief products were denoted by Schardinger dextrin- α and dextrin- β , and of these the α -derivative was found to preponderate.

When a 5 p.c. starch paste is inoculated with *B. macerans* from a potato culture, at 37° – 48° , liquefaction takes place in 24 hours, whilst the fermentation which accompanies it gives rise to copious evolution of gas. In 6–7 days fermentation is nearly at an end. The optimum hydrogen ion concentration for this organism is $P_H=6.8$. To the liquid fermentation product

was added different organic solvents, *e.g.* chloroform, ether, benzene, toluene, xylene, bromobenzene, nitrobenzene, or light petroleum. With any one of these a crystalline paste was obtained which was dissolved in a little water and the organic precipitant boiled off. A precipitate separated which Schardinger designated as a slime, whilst by concentrating the filtrate a crystalline product was obtained, dextrin- β . The main product, dextrin- α , was, however, obtained from the filtrate by precipitation with alcohol. A crystalline dextrin was also obtained from the slime by crystallising it from dilute alcohol. These dextrans do not reduce Fehling's solution, and they are not fermentable by yeast. Pringsheim and Langhans show that these three dextrans have the following molecular formulæ: dextrin- α $(C_6H_{10}O_5)_4$, dextrin- β $(C_6H_{10}O_5)_6$, whilst the dextrin from the slime was first thought to have the formula $(C_6H_{10}O_5)_8$, but it has since been shown that its formula is



(*cf.* further, under *Amyloses*, below).

16. *The amyloses*.—H. Pringsheim with A. Langhans and F. Eissler (Ber. 1912, 45, 2533; 1913, 46, 2959) suggest the generic term amylose for polysaccharides of the formula $(C_6H_{10}O_5)_n$. Of the crystalline dextrans (*see* above), dextrin- β , which decomposes at 268° , is too sparingly soluble in water for accurate cryoscopy, but dextrin- α (tetra-amylose), decomposing at 292° , proves to have a molecular weight, $(C_6H_{10}O_5)_4$. Both forms are acetylated by acetic anhydride in the presence of zinc chloride, but scission of the molecules occurs at the same time; dextrin- α yields the hexa-acetyl derivative of a diamylose, needles (decomp. 151.5° – 152.5° , $[\alpha]_D$ 100.6° in acetic acid), whilst dextrin- β gives the nona-acetyl derivative of a triamylose (tablets, decomp. 142° , $[\alpha]_D$ 112.6° in acetic acid). Hydrolysis of these acetyl derivatives by cold alcoholic potassium hydroxide produces respectively diamylose $(C_6H_{10}O_5)_2$ (decomp. about 300° , $[\alpha]_D$ 136.2° in water), which crystallises from water in needles with $2H_2O$, and triamylose, $(C_6H_{10}O_5)_3$, needles, crystallising with $4H_2O$, decomposing near 300° ; $[\alpha]_D$ 151.8° in water. These amyloses give green or reddish-brown, crystalline iodine additive compounds, which dissolve to dark red solutions, and they are not attacked by diastase, saliva, pancreatin, or emulsin, but are hydrolysed by takadiastase and *Penicillium africanum*. According to the work of P. Karrer and C. Nacgeli (Helv. Chim. Acta, 1921, 4, 169, 185, 263) diamylose is simply an anhydride of maltose and methylated starch $[C_{12}H_{16}O_6(OMe)_4]_x$, has a molecular weight of at most 1200. The aqueous solution of this substance shows the Tyndall effect, but after ultra-filtration with little loss it is optically void and truly crystalloidal. The conclusion is drawn that the starch molecule contains not more than six dextrose residues united by chemically normal linkings, that is, that it is hexa-amylose polymerised by subsidiary valencies; and that it is related to the amylose as a crystal is to a single molecule. H. Pringsheim and W. Persch (Ber. 1921, 54, [B], 3162) conclude from a study of tetra-amylose that by Haworth's

method two hydroxyl groups per hexose residue are methylated without causing depolymerisation, and molecular weight determinations show that it is octamethyl tetra-amylose. It crystallises in colourless hexagonal plates which do not decompose below 250° . Its specific rotatory power in alcoholic solution is $[\alpha]_D$ 141.5° – 148.2° . The slight muta-rotation is surprising, since the original tetra-amylose is not muta-rotatory. Fermentation of starch by a degenerated specimen of *Bacillus macerans* has led to the isolation of a tetra-amylose which gives a dark green, crystalline, additive compound with iodine, and after being freed from the latter, a crystalline, additive product with carbon bisulphide. Removal of the latter gives a tetra-amylose crystallising in needles and having a specific rotation higher by a few degrees than that quoted for previous specimens. The substance is possibly a stereoisomere, but its preparation is difficult and uncertain.

In a later paper (*ibid.* 1921, 55, 1425) the authors show that octamethyltetra-amylose is readily converted by acetic anhydride and pyridine into the corresponding tetra-acetyl derivative $(C_6H_7O_5(CH_3)_2(CH_3CO)_4)$, hexagonal rods, which darken without melting at 120° , $[\alpha]_D^{20}$ 118.62° in ethyl alcohol. Diamylose resembles tetra-amylose in that it is converted by successive treatment with methyl sulphate and sodium hydroxide and methyl iodide and silver oxide into tetramethyldiamylose, hexagonal plates, which do not melt below 200° , $[\alpha]_D^{20}$ 143.74° in ethyl alcoholic solution. Attempts to methylate the third hydroxyl group were unsuccessful. The behaviour of the polyamyloses of the β -series towards methylation is peculiar. With hexa-amylose, reducing action towards Fehling's solution is observed after a single treatment with methyl sulphate and sodium hydroxide, although the solution was not at any time acid. With triamylose, the phenomenon was first noticeable after the first methylation with silver oxide and methyl iodide and became more marked after a second treatment with the same reagents.

The author's method of acetylation with acetic anhydride and pyridine permits without depolymerisation the conversion of the slimes obtained by the degradation of starch with *Bacillus macerans*, into hexa-amylose dodeca-acetate, aggregates of minute needles. It shrinks at 135° , but does not melt definitely below 215° , $[\alpha]_D^{20}$ 95.77° , when dissolved in glacial acetic acid. It is converted by alcoholic potassium hydroxide solution into the initial material, which is thus characterised as a α -hexa-amylose.

H. Pringsheim and D. Dernikos (*ibid.* 1433) find that when α -tetra-amylose is acetylated it yields a dodeca-acetate, $[C_6H_7O_2(OCH_3CO)_3]_4$, needles, $[\alpha]_D^{18}$ 115.8° in glacial acetic acid solution, the molecular weight of which has been determined in benzene and bromoform. It is reconverted by alcoholic potassium hydroxide solution into α -tetra-amylose, the identity of which is established by the determination of its molecular weight. The application of this

method of acetylation to polyamyloses of the β -series has led to surprising results, since β -hexa-amylose is thereby converted into the same triamylose nona-acetate, $[\text{C}_6\text{H}_7\text{O}_2(\text{OCH}_3\text{CO})_3]_3$, $[\alpha]_D^{16}$ 117.9° in glacial acetic acid solution, as was obtained previously by acetylation in the presence of zinc chloride; a possible explanation of the unexpected depolymerisation is found in the fact that the experimental conditions, by reason of the sparing solubility of the initial material, were necessarily more drastic than those adopted with the members of the α -series.

Karrer has recently expressed the opinion that β -hexa-amylose is not depolymerised by acetylation in the presence of zinc chloride, in which case Pringsheim's triamylose must be merely de-acetylated β -hexa-amylose. Reasons are advanced for considering that data obtained from the action of acetyl bromide on polysaccharides are unsatisfactory in the quantitative form given to them by Karrer. The compounds of triamylose with the alkali hydroxides have, according to Karrer, the formula $\text{C}_{12}\text{H}_{20}\text{O}_{10}\cdot\text{NaOH}$. It is pointed out that a compound prepared in accordance with Karrer's directions by the precipitation of a solution of β -hexa-amylose in aqueous sodium hydroxide (10 p.c.) with alcohol had the composition $(\text{C}_6\text{H}_{10}\text{O}_5)_3\cdot\text{NaOH}$, but great value cannot be placed on the results of analyses of these substances, since their alkali content is greatly dependent on the experimental conditions. Hydrolysis of triamylose acetate with sodium ethoxide followed by thorough washing of the precipitate with absolute alcohol gives a substance $(\text{C}_6\text{H}_{10}\text{O}_5)_3\cdot\text{NaOH}$. Contrary to Karrer's observations, β -hexa-amylose invariably contains a higher percentage of water of crystallisation than triamylose. The solubilities of the two substances in water are not identical; as concordant results of two different methods the solubility of triamylose in water at 20° is 1.3 p.c. by weight and 1.34 p.c. by volume, the corresponding figures for β -hexa-amylose being 2.4 and 2.65. Contrary to Karrer, the optical activity of triamylose is lower than that of β -hexa-amylose. A revision of the crystalline forms of triamylose and β -hexa-amylose confirms Karrer's observation of their identity. Attempts to determine the molecular weight of triamylose in boiling water were unsuccessful, since a true solution could not be obtained. Measurements of the crystals of diamylose, triamylose, and β -hexa-amylose, tetra-amylose, and α -hexa-amylose are recorded.

Glycogen is also regarded as a polymerised amylose, differing from starch in the degree of polymerisation. Karrer and Naegeli (Helv. Chim. Acta, 1921, 4, 169, 185, 263) believe the molecular weight of starch to be much smaller than it has been supposed to be by various authors, for instance, M. Samec and H. Haerdtl (Koll. Chem. Beihefte, 1920, 12, 281), who have recorded enormous molecular weights for different varieties of starch, up to 260,000.

The amyloses isolated by Pringsheim and his collaborators are shown in the following table, the basal molecules being within round brackets, whilst the polymeric molecule are within angular brackets:—

	α -Series	Specific Rotation
α -Hexa-amylose (from the slime)	$[(\text{C}_6\text{H}_{10}\text{O}_5)_2]_3$	$[\alpha]_D$ 139°
α -Tetra-amylose (from dextrin- α)	$[(\text{C}_6\text{H}_{10}\text{O}_5)_2]_2$	„ 136.8°
Diamylose	$(\text{C}_6\text{H}_{10}\text{O}_5)_2$	„ 136.6°
β -Hexa-amylose (from dextrin- β)	$[(\text{C}_6\text{H}_{10}\text{O}_5)_2]_3$	„ 157.9°
Triamylose	$(\text{C}_6\text{H}_{10}\text{O}_5)_3$	„ 151.8°

Pringsheim and his collaborators consider that starch and the polyamyloses consist of basal units polymerised to different degrees, the units being held together by subsidiary valencies. The polymeric substances may therefore be regarded as co-ordination compounds.

Karrer and Bürklin (Helv. Chim. Acta, 1922, 5, 181) believe that β -hexa-amylose consists of trimaltose anhydride $(\text{C}_{12}\text{H}_{20}\text{O}_{10})_3$. Support for this view is afforded by the observation of Karrer and Naegeli (Helv. Chim. Acta, 1921, 4, 169), that by the action of acetyl bromide on the polyamyloses in presence of a little glacial acetic acid, hepta-acetylbromomaltose is produced, from which maltose may be obtained when it is shaken with silver carbonate and the product hydrolysed.

Picht and Jahn (Helv. Chim. Acta, 1922, 5, 640) find that when starch is dissolved in glycerol and the solution heated at 200°–210° for $\frac{3}{4}$ hour, and the glycerol removed by distillation, at 2–4 mm. a white amorphous substance $(\text{C}_6\text{H}_{10}\text{O}_5)_3$ is obtained to which they give the name *tri-hexosan*. It gives no coloration with iodine, and does not reduce Fehling's solution. It decomposes at 230°–232°, and its specific rotatory power is $[\alpha]_D$ 162.1°–162.3°.

P. Karrer and W. Fioroni (Ber. 1922, 55, [B], 2854) have redetermined the heats of combustion of the amyloses with the following results expressed in calories per gram. of substance: diamylose (4285), α -tetra-amylose (4196), α -octa-amylose (4620), β -hexa-amylose (4166), lævoglucozan (4181), triamylose (identical with β -hexa-amylose) (4172.5). Polymerisation proceeds exothermally from diamylose to α -tetra-amylose and then strongly endothermally to octa-amylose. In further examination of the possibility of calculating the heat of combustion of a sugar of the general formula $(\text{C}_6\text{H}_{12}\text{O}_6)_n + \text{H}_2\text{O}$, the values have been determined experimentally for cellobiose (3944) (calculated from the observed value for a specimen containing 2.2 p.c. of water), sucrose (3945), lactose (3953), and maltose (3949); within the limits of experimental error, these disaccharides, $\text{C}_{12}\text{H}_{22}\text{O}_{11}$, have identical heats of combustion. This is also true of maltose octa-acetate (4468) and cellobiose octa-acetate (4471). The observed and calculated values for the trisaccharide, raffinose, have been shown to be in harmony, and similar observations are recorded for the tetrasaccharide, stachyose (observed 4065, calculated 4058).

The dependence of the heat of combustion on the degree of polymerisation is illustrated in the case of the α -amyloses. A comparison of the heats of combustion of acetyl-cellulose, -starch, and -inulin on the one hand and the

non-acetylated polysaccharides on the other should therefore give valuable information as to the possibility of the acetylation being accompanied by depolymerisation. The observed values are as follows: inulin (4190), starch (4182), cellulose (4185), starch hexa-acetate (4499), cellulose hexa-acetate (4496), inulin triacetate (4522). The heats of combustion of the acetates are calculated from those of the parent substances on the assumption that the heat of esterification (known to be small) can be neglected. The observed and calculated values agree so closely that there is no reason to suppose that an alteration of the degree of polymerisation of the carbohydrate occurs during acetylation.

Karrer contends that hexa-amylose is identical with tri-amylose, and his observations have been confirmed by the crystallographical measurements of Miggle and Johnson. The individuality of the substances has, however, been maintained by Pringsheim, to whose arguments a critical reply is now given. Pringsheim's doubt as to the identity of the supposed heptacetyl derivative of maltose obtained by the action of acetyl bromide on triamylose is unjustified, since it is a well-defined, crystalline substance. Attempts to repeat the preparation of triamylose sodium hydroxide according to Pringsheim's method gave a product which contains sodium ethoxide. Contrary to Pringsheim's observations, the solubilities of triamylose and hexa-amylose in water are identical, and the observed discrepancies are due to the inadequacy of Pringsheim's method of experiment. With regard to Pringsheim's observation that the molecular weight of acetylated hexa-amylose is identical with that required for an acetylated triamylose, the author points out that acetylated anhydro-sugars are not in general suitable for determinations of molecular weight; incidentally, the molecular weight of acetylated hexa-amylose, as determined by Rast's method (Ber. 1922, 55 [B], 1051), is about 1950 (or exactly double that found by Pringsheim). Doubts are cast on the individuality of Pringsheim's trifructose.

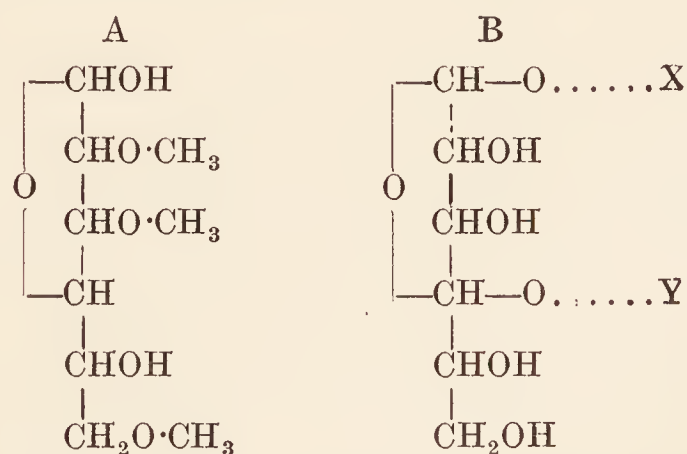
17. *Constitution of starch.*—J. C. Irvine and J. Macdonald (Brit. Ass. Sectional Address, 1922, 16; also Trans. Chem. Soc. 1923, 123, 898) have published a preliminary report on their work on this subject, of which the following is an abstract. They worked on purified rice starch and recognise that their results apply to it only. They postulate that the molecule of starch consists entirely of glucose groups, and that three hydroxyl groups are present for every six carbon atoms. This does not necessarily imply that each glucose residue contains three unsubstituted hydroxyl groups, or that their distribution is symmetrical; but that it is an essential point that a structural formula should be consistent with the production of maltose. The authors state that at the present time the view prevails that starch is derived from a comparatively simple anhydro-sugar by profound polymerisation. The unit of starch has been claimed to be β -glucosan (Pictet, p. 347); anhydro-maltose (Karrer, Natur. wiss. 1921, 9, 399); triamylose (Pringsheim, Zeitsch. angew. Chem. 1922, 53, 345).

The views put forward by the three chemists cited have been tested by the methylation method.

When starch is methylated by Haworth's method, treatment with dimethyl sulphate in presence of alkali (Trans. Chem. Soc. 1915, 8), the reaction ceases when the methoxyl content is 37 p.c. It is to be noted that this maximum is not reached when the silver oxide and methyl iodide reaction is employed, as the substitution then stops definitely at the dimethyl stage. Now, the higher value for methoxyl corresponds exactly with the theoretical amount calculated on the basis that one hexose residue has acquired three methyl groups, while four are shared by two glucose residues. Ultimate analysis is also in agreement with this view. Hydrolysis of the methylated starch has shown that this is not a fortuitous coincidence, and there is thus obtained a direct clue to the magnitude of the unit which goes to form the starch molecule. When digested with methyl alcohol containing hydrogen chloride, the methylated polysaccharide was converted into trimethyl methylglucoside and dimethyl methylglucoside. These were purified by distillation in a high vacuum, and thereafter hydrolysed to give the parent sugars. A totally unexpected result was encountered in that the trimethyl glucose actually isolated proved to be the crystalline form in which the methyl groups occupy the 2, 3, 6-positions.

It will be seen that the removal of trimethyl glucose and dimethyl glucose in the molecular ratio of 1:2 is effected without alteration in the composition of any methylated starch which survives hydrolysis. The result is striking confirmation of the view that starch is based on an anhydro-trisaccharide in which two hexose residues are linked in a different fashion from the third. One of these is constituted as in formula B, and the remaining two must be added in such a way that at least one pair displays the essential structure of maltose (Purdie and Irvine, Trans. Chem. Soc. 1905, 1022).

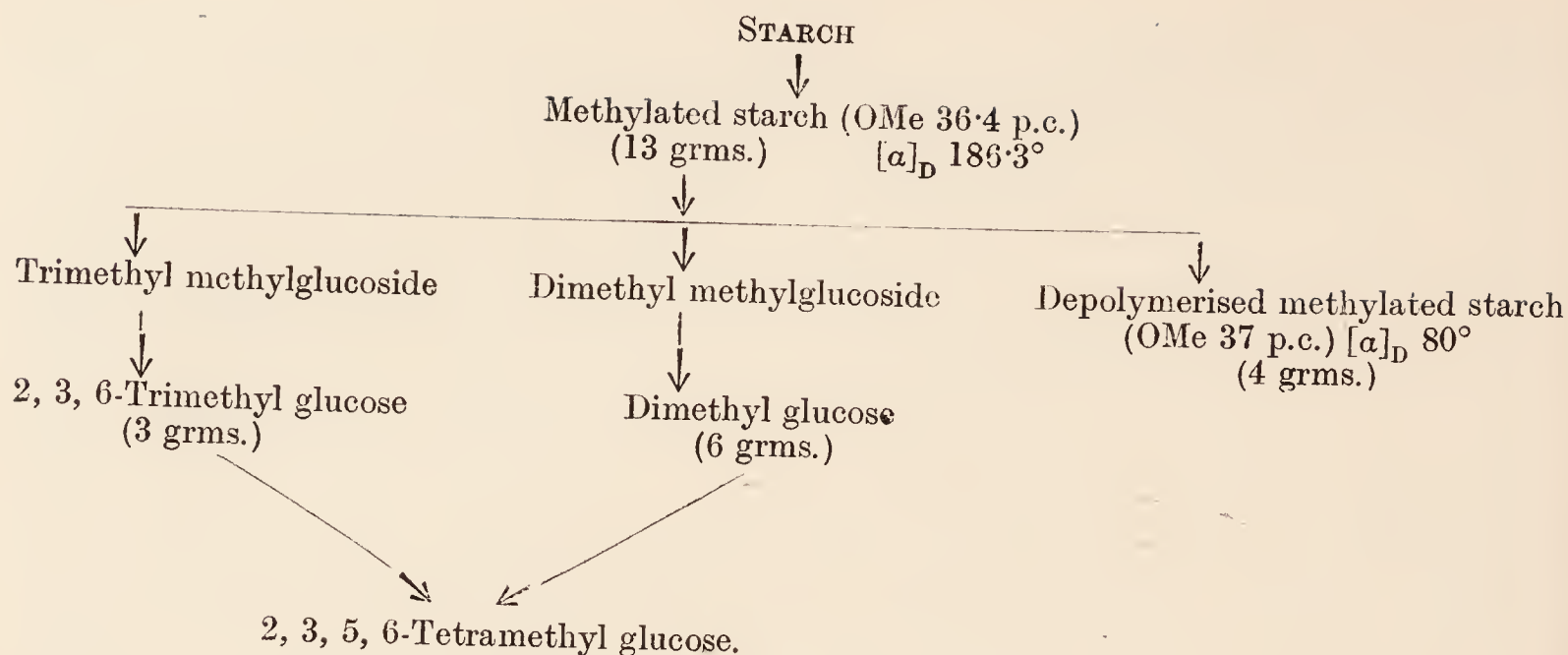
This methyl derivative has been shown to have the constitution shown in formula A, whilst the linkage of one glucose unit in the starch molecule is shown in formula B.



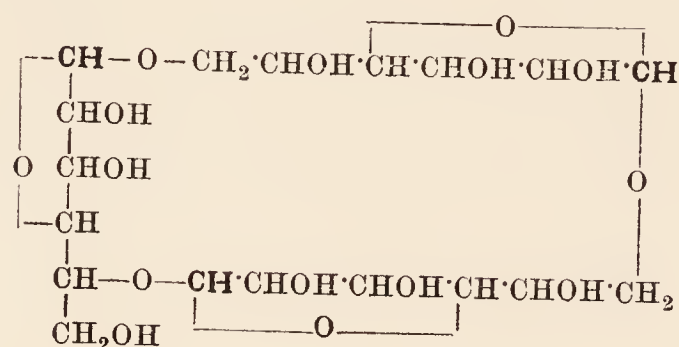
It is to be noted that this particular type of structure is not present in maltose, but is characteristic of cellobiose and lactose.

In order to accommodate the formation of maltose from starch, either one or two additional glucose residues must be present at X and Y in the unit. Before developing a formula which will fulfil the above conditions an outline of the reactions involved may be given:—

STARCH.



Four different structures may be built up to accommodate these facts, and of these preference is given by Irvine and Macdonald to the following:—



(Letters in block type designate the potential reducing groups.)

One objection may, however, be discussed. In the formation of maltose no more than one molecule of this disaccharide could be obtained from one such unit. The maximum yield of the sugar would therefore be of the order 70 p.c. (74 p.c. calculated as maltose hydrate). Yields higher than this figure are quoted in the literature, but it may be remarked that most specimens of maltose do not behave as identical homogeneous chemical individuals in bacteriological tests. Further, von Euler and Svanberg (*Zeitsch. physiol. Chem.* 1921, 112, 207), who conducted the diastatic hydrolysis of starch under conditions in which the optimum hydrogen ion concentration was present, report that the yield of maltose formed is then 75 p.c.

It may be pointed out that the experimental results now presented demand the rejection of various formulæ for starch proposed from time to time by Karrer. His structures are based on a diamylose (anhydro-maltose), two formulæ for which have been put forward differing in the position of the anhydro-ring. The evidence he adduces in favour of these views is not convincing. The work of Irvine and his collaborators has thrown light on various other problems connected with the chemistry of starch, including the attachment of nitrogen and phosphorus to the molecule. These elements do not appear to be constituents of extraneous compounds, but form part of the polymerised aggregate. This is shown very clearly by the behaviour of nitrogenous starch, which was methylated in the first instance by the use of methyl sulphate and alkali. Thereafter the product was treated with silver oxide

and methyl iodide, but contrary to expectation, the whole of the material became converted into an insoluble additive compound with silver iodide. This behaviour does not extend to a purified starch, and finds an exact parallel in the case of glucosamine derivatives, which, under identical conditions, form insoluble complexes with silver halides (Irving and Hynd, *Trans. Chem. Soc.* 1912, 1128). Obviously if nitrogen were present merely as part of an adventitious impurity only this component would be removed in the course of the silver oxide alkylation, and the fact that the total material was precipitated is a proof that the fragment containing nitrogen is definitely polymerised to the starch unit. Similar considerations apply to the case of glycogen, and have served to complicate our work on the alkylation of this compound.

Ling and Nanji (*Trans. Chem. Soc.* 1923, 2666) have published some work on the nature of polymerised amylose and of amylopectin (see p. 345). They believe polymerised amylose to consist of a basal unit of α -hexa-amylose $[(C_6H_{10}O_5)_2]_3$ (see formula I, p. 366), and amylopectin to consist of α - β -hexa-amylose $[(C_6H_{10}O_5)_3]_2$ (see formula III, p. 367). Amylopectin as it exists in the starch granules appears to consist of polymerised α - β -hexa-amylose existing as a phosphoric ester, and it is pointed out that the conversion of ordinary potato starch into soluble starch by treatment with 7 p.c. hydrochloric acid, according to Lintner's method (see p. 348), consists in the hydrolysis of this phosphoric ester, since phosphoric acid is to be found in the hydrochloric acid used for treating the starch. Amylose as it exists in the starch granules appears to consist of polymerised α -hexa-amylose.

Clayson and Schryver, and Schryver and Thomas (*Bio-Chem. J.* 1923, 493, 497) have pointed out that starches of sago, maize, tapioca, wheat, and rice contain a hemicellulose, and Ling and Nanji have confirmed this in the case of the starches of wheat, barley, and rice, the only ones they examined. They find also in confirmation of the observations of Schryver and his co-workers, potato starch does not contain this constituent. The hemicellulose would seem to exist as an ester of silicic acid, but this matter is still under investigation.

It is shown that when potato starch paste is

subjected to the temperature of a mixture of ice and salt, it is precipitated completely. If the mass is subsequently raised to the ordinary temperature, the amylose dissolves, and if the solid matter be washed with water or dilute alkali and the temperature brought just below the gelatinising point of the starch, it is possible to remove the whole of the amylose from the amylopectin, which then presents the appearance of a wad of moist cotton wool. When potato starch paste is treated at 50°C. with barley grist, or barley extract, or a solution of freshly precipitated barley diastase which has not been dried by treatment with strong alcohol, the amylose is converted completely into maltose, whilst the amylopectin is partially depolymerised to the substance previously described by Baker as α -amylodextrin (see p. 360). This substance has been obtained devoid of reducing power, which represents the first stage in the depolymerisation of amylopectin, the final stage being α - β -hexa-amylose. Polymerised α - β -hexa-amylose in either of its forms gives with iodine a bluish-black precipitate or a clear blue solution, according to the concentration of the polysaccharide. Precipitated barley diastase which has been dehydrated with alcohol and dried does not possess the power of attacking amylopectin to any extent, and is therefore recovered almost unchanged, having a specific rotatory power of about $[\alpha]_D = +221^\circ$. Treated with malt diastase at 70° until it ceases to give an iodine reaction, it is converted into a hexatriose, which is shown to be α -glucosidoisomaltose or β -glucosidomaltose. This sugar has been obtained as a white hygroscopic powder melting sharply at 202°–203°. Its specific rotatory power is $[\alpha]_D = 165^\circ$, and reducing power R 66. It forms an osazone which is very soluble in water and crystallises therefrom in rosettes of minute needles, melting at 122°. When the hexatriose is submitted to the action of β -glucosidic enzyme prepared from bitter almonds, it is hydrolysed, giving a mixture of glucose and maltose. On the other hand, when it is submitted to the action of yeast maltase or malt diastase, glucose and isomaltose are obtained. Ling and Nanji have definitely settled the existence of isomaltose amongst the products of hydrolysis of starch by malt diastase. They point out that as long as studies were confined to the action of malt diastase on starch it was practically impossible to settle the question, since by that enzyme both polymerised amylose and amylopectin are hydrolysed, giving rise to a mixture of maltose and isomaltose which are difficult to separate by fractionation with alcohol. It is different when resort is had to an enzyme which only saccharifies polymerised amylose, such as dry precipitated barley diastase. When the last-mentioned enzyme is allowed to act on starch, the products are maltose and partially depolymerised amylopectin. Under these conditions Baker observed in one experiment a reducing power as high as 66.6 p.c. expressed as maltose. Ling and Nanji have observed a reducing power as high as 70 p.c. expressed as maltose. The conditions were so adjusted in this case that no glucose was produced (cf. Ling and Nanji, Bio-Chem. J. 1923, 17, 593).

Many observers have claimed that potato

starch paste under the influence of malt diastase is completely converted into maltose. Thus Ling and Davis (J. Inst. Brewing, 1902, 8, 475), employing malt diastase, show that the starch of potato, maize, and rice, when hydrolysed with precipitated malt diastase at 55° for a prolonged period, gave conversions, the dissolved solids of which have the following constants:—potato $[\alpha]_{D^{3.93}} = 138.5$, $R_{3.93} 96.7^\circ$; maize $[\alpha]_{D^{3.93}} = 139.4^\circ$, $R_{3.93} 96.7$; rice $[\alpha]_{3.93} 139.4^\circ$, $R_{3.93} 96.1$.

Ling and Davis state that in such solutions they were able to detect nothing but maltose. It will be noticed, however, that the reducing powers are all below 100, and if it be assumed that starch under the action of malt diastase yields ultimately a solution containing a mixture of approximately 80 p.c. of maltose and 20 p.c. of isomaltose, the constants of such a solution should be $[\alpha]_D = 138$, $R 96$, values which agree closely with those of Ling and Davis. In fact Ling (Brit Assoc. Report, Southport, 1903) states that potato starch paste is never completely converted into maltose by the action of malt diastase, and that a substance is always present which is identical with the isomaltose of Lintner. Since Lintner and other workers separated isomaltose from the products of the action of malt diastase on starch paste, the preparations were always of very uncertain purity. Still it is remarkable that Lintner's preparations gave the true constants for isomaltose. This sugar is conveniently prepared by the following method. Crude amylopectin or polymerised α - β -hexa-amylose is treated with precipitated malt diastase at 50° until the rotatory power remains constant. The solution is next fermented with yeast, and after the termination of the fermentation the yeast is filtered off, the solution decolorised with Norit and evaporated under diminished pressure to a thick syrup which is taken up by boiling 90 p.c. alcohol, when mineral matters, proteins, &c., remain undissolved. The alcoholic solution is then concentrated at a low temperature, when the sugar is obtained as a white amorphous, fairly hygroscopic powder. It does not possess any definite melting-point, nor can it be induced to crystallise. It has a sweeter taste than maltose, a fact to which Lintner has already directed attention. The specific rotatory power of the pure sugar ($c=3-4$) is $[\alpha]_D = 140^\circ$, and the reducing power R 80. It forms a phenyl-osazone, melting at 152°. It is unfermentable by *Saccharomyces Cerevisiae*. The conclusions arrived at by Pringsheim, Karrer, Pictet, and Irvine are discussed by Ling and Nanji.

In three further papers by Ling and Nanji (Trans. Chem. Soc. 1925, 629, 636, 652) the study of the constitution of the constituents of starch and their products of hydrolysis has been continued. It has been found that polymerised α -hexa-amylose can be obtained from frozen starch paste in a yield of 15–17 p.c. on the dry starch. All starches, however, are shown to contain polymerised α -hexa-amylose and amylopectin in the ratio of 66.6–33.3 parts. The amylose is present in two forms, crystalloidal, which may be extracted as already mentioned, and colloidal, which latter exists as a co-ordinated mixture in association with amylo-

pectin. In both its forms amylose is readily hydrolysed by either barley or malt diastase at 50° , yielding exclusively maltose without the production of any intermediate products. These enzymes are practically without action on the amylose at 70° . The optimum temperature of hydrolysis with barley diastase is 45° . The relative quantities of polymerised α -hexa-amylose and of amylopectin in different starches have been determined by a method based on the complete conversion of the former into maltose by barley diastase.

The constitution of the hexatriose derived from amylopectin (see Fig. 1) is found to be β -glucosido-maltose (see Formula II). From this fact, together with other considerations, the constitution of α - β -hexa-amylose has been deduced (see Formula III).

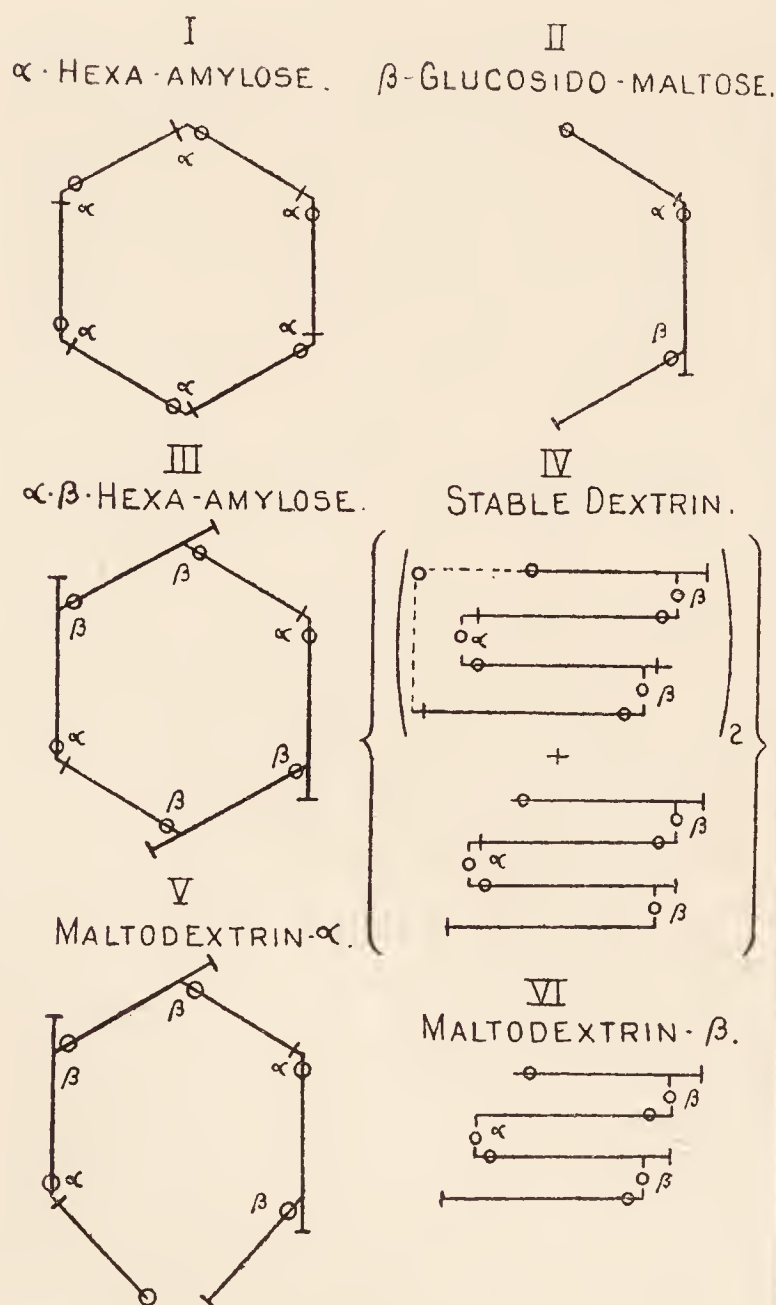


FIG. 1.

When α - β -hexa-amylose is hydrolysed by malt diastase in presence of maltose (66 p.c.), an apparent resting stage is reached corresponding to the stable dextrin equation of Brown and Morris. This resting stage is not observed when α - β -hexa-amylose is hydrolysed alone, the optimum temperature being 50° . The production of glucose among the products of hydrolysis at 70° is shown to be due to the formation of β -glucosido-maltose, which further breaks down into isomaltose, or maltose, and glucose. The stable dextrin is found therefore to be a derivative of α - β -hexa-amylose, and it has been

isolated exactly in the form in which it exists in a starch conversion brought to the resting stage. It has the constants $[\alpha]_D^{185}$ and R 14. It is derived from α - β -hexa-amylose by the conversion of one-third its weight into maltose. The basal unit is thus a C_{24} complex consisting of a coordinated mixture of maltodextrin- β (Ling and Baker, p. 356), and the corresponding tetra-amylose in the ratio 1:2. The optimum temperature for the hydrolysis of the stable dextrin with malt diastase is 40° . With maltase at this temperature it yields isomaltose, and with emulsin, maltose and glucose. From these facts the constitution of the stable dextrin has been deduced (Formula IV). Maltodextrin- α (Ling and Baker, p. 356) (Formula V) is produced by the opening of one of the linkages in the α - β -hexa-amylose ring when the latter is hydrolysed with malt diastase at 70° . The terminal carbinol and carbonyl groups are in the isomaltose and maltose residues respectively. Maltodextrin- β (Ling and Baker, p. 356) (Formula VI) has similarly been shown to be produced from α - β -hexa-amylose by the elimination of one-third its weight of maltose. The carbinol and carbonyl groups in malto-dextrin- β are in the maltose and isomaltose residues respectively of the chain.

A method has been devised for the isolation and estimation of the hemicellulose constituent of certain starches, consisting in treating the starch paste with barley diastase. This treatment leaves the hemicellulose unattacked, and since it is insoluble in cold water it may be separated from the soluble products. It gelatinises with boiling water, and when the paste is treated with malt diastase it is, like α -hexa-amylose, rapidly hydrolysed to maltose, the optimum temperature being 50° - 55° ; malt diastase at 73° is without action, in which it also resembles α -hexa-amylose, of which it is shown to be a silicic ester.

The behaviour of the different constituents of starches towards barley and malt diastase and the relation of their products of hydrolysis are shown in Figs. 1-3.

MANUFACTURE OF STARCH.

18. *General considerations.*—This industry is one of considerable antiquity, as there are records relating to it dating back some hundreds of years. As may be expected, considerable progress in recent years has been made on the technical side, and the processes as now conducted in Europe and America leave little room for improvement. Apart from its historical interest, the industry is one of considerable magnitude, more especially if we include the starch separated from the particular cereal, but not marketed as such; that is to say, obtained as a preliminary process in the manufacture of glucose or alcoholic liquor. The figures given later are a sufficient index to the importance of the industry. In the early days of starch manufacture, the starch was prepared almost exclusively from wheat, but during recent times, partly owing to the special characteristics of particular starches, and partly for economic reasons, starches from other sources have predominated; as from maize,

potato, rice, and cassava. In the manufacture of glucose, etc., there is no necessity to use a particular kind of starch, and the choice is governed very largely by the price of the starch or starch-bearing grain or tuber. On the other hand, for laundry purposes, and to some extent for the textile trade, economic reasons are a secondary consideration, the demand being based upon the characteristics of the starch; rice starch for the laundry, and potato or maize

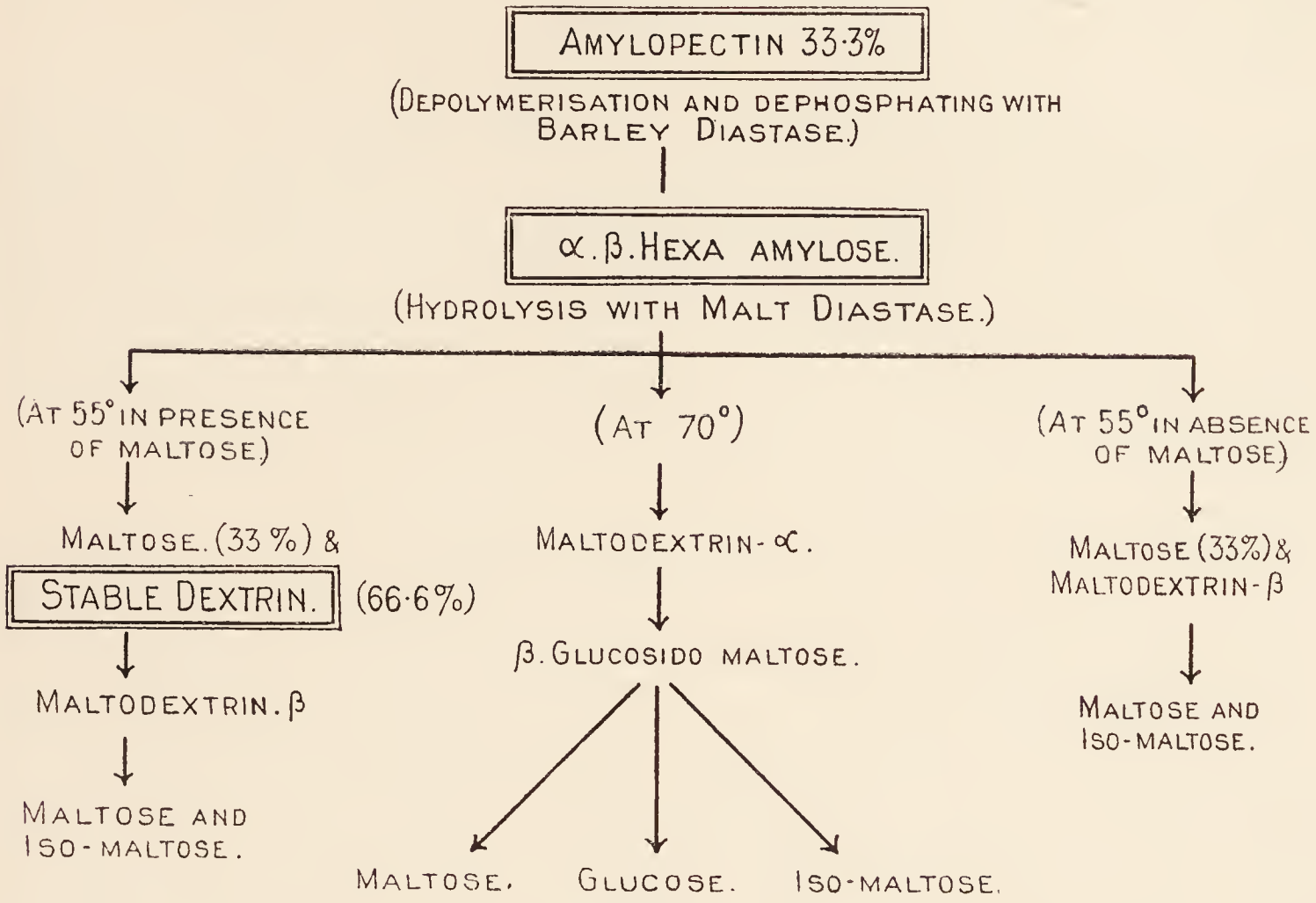


FIG. 2.

for the textile trade. For the manufacture of the best quality dextrin—a Dutch and German industry—potato starch is essential. In addition there is a considerable consumption of starch as a food, and arrowroot, sago, and especially refined maize, each have their particular uses. The percentage of starch in the raw materials varies considerably, as the following table will indicate, and in the case of the potato a good deal of attention has been given to increasing the starch content with considerable success:—

	Wheat	Maize	Rice	Potato	Cassava
Percentage starch in .	68	69	78	18	20

The yield of starch per acre also shows great variation, the average figures being—

	Wheat	Maize	Rice	Potato	Cassava
Lbs. of starch per acre .	1140	1100	740	4032	5370

As might be expected, the manufacture of any particular starch has largely centred where the starch-bearing material is grown extensively and cheaply, with the result that in the U.S.A. maize starch, on the Continent of Europe potato, in the tropics or sub-tropics arrowroot, sago, and cassava, are produced. Rice starch is not produced where grown, and the industry is practically confined to Germany, Belgium, Austria, Holland, and England. Some maize starch is produced in the United Kingdom, but not so much as formerly.

APPROXIMATE PRODUCTION OF STARCH (TONS).

	U.S.A.	Europe	Tropics and sub-Tropics
Maize . .	150,000	25,000	—
Potato . .	10,000	100,000	—
Rice . .	—	50,000	—
Cassava, Arrowroot, Sago, &c. }	—	—	50,000

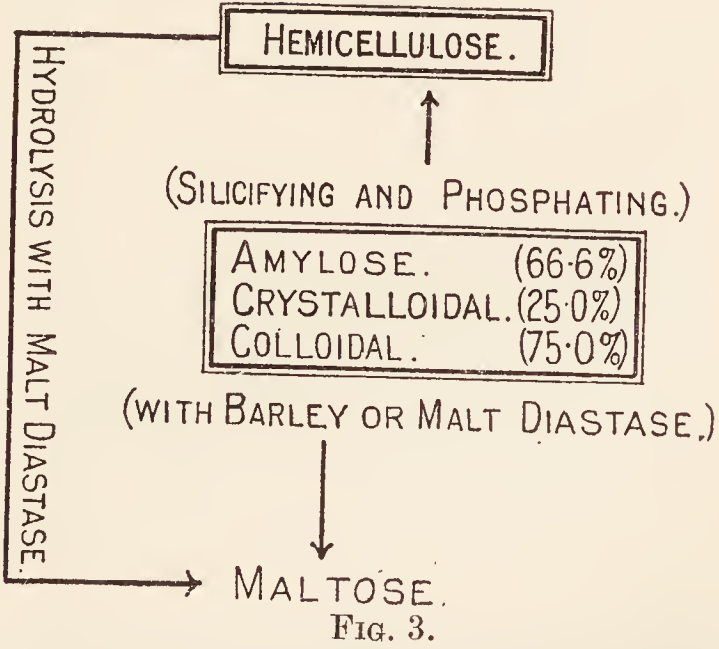


FIG. 3.

These figures do not include starch produced as a preliminary to a subsequent conversion product. The following table shows the imports of starches to the United Kingdom for 1920, 1921, and 1922:—

STARCH IMPORTS INTO UNITED KINGDOM.

For the years 1920, 1921, 1922.

	1920 cwts.	1920 £	1921 cwts.	1921 £	1922 cwts.	1922 £
Rice starch . .	44,728	155,380	62,242	116,925	87,573	136,628
Other kinds . .	949,599	1,881,657	1,030,099	856,079	1,621,286	1,048,724
Dextrin, farina, or potato flour . }	619,360	1,212,615	446,930	528,947	647,041	714,908
Total . .	1,613,687	3,249,652	1,539,271	1,501,951	2,355,900	1,900,260

Starch was extracted from wheat and barley by the ancient Egyptians, Greeks, and Romans. It was called *ἄμυλον* by the Greeks, from the circumstance of its not having to be prepared by the action of grinding in mills like other farinaceous substances, whence the Latin *amylum*. Very little, however, appears to have been known about its history or composition until the beginning of the 18th century.

19. *Manufacture of starch from wheat.*—The different methods of preparing starch from wheat are

I. By fermentation, known as the old or sour process.

II. Without fermentation, or Martin's process.

I. Fermentation process. For the old method the wheat is used either whole or ground, but most frequently whole.

Where the whole corn is employed, the wheat is steeped in soft water for some days, until it becomes swollen and so soft as to be easily crushed between the fingers; the water being changed frequently, so as to ensure, at the same time, a thorough washing of the grain. The swollen corn is now transferred to bags, and placed in a wooden chest or flat tub, where it is exposed to strong pressure. By this means the grains are crushed, and the water, which is rendered milky by the starch, is drawn off by means of a tap; fresh water is poured in, and the pressure repeated until all or nearly all of the starch is extracted. Instead of putting the swollen grain in bags, it may be passed from a hopper between two wooden cylinders revolving in opposite directions, or between one or two cylinders revolving upon a horizontal stone having a rim, to a cistern; by this means the swollen corn is readily crushed and the starchy liquor in the cistern separated by elutriation with successive quantities of water.

The milky liquor containing the starch is next run into cisterns, where it is allowed to remain for a period of from 10 to 30 days, according to the temperature of the surrounding atmosphere, during which time it undergoes fermentation, in order to accelerate which some of the sour liquor from a previous fermentation is added.

By this means the starch granules become completely freed from the glutinous envelopes containing them in the grain, the gluten becomes more or less decomposed and softened, and partially dissolved in the acids formed during the process, and completely loses its sticky elastic properties.

During the earlier stages of the fermentation the ready-formed sugars of the grain, as well as dextrin resulting from the action of the diastase on any broken starch granules, become converted into alcohol, which later on is changed into acetic acid; after a few days lactic, butyric,

and other fermentations are set up, and allowed to proceed until the process is considered sufficiently far advanced to allow of the starch granules being easily separated in a state of comparative purity. As a rule, actual putrefaction, as shown by the evolution of stinking gases, should be avoided as much as possible, and the fermenting mass should always have an agreeable vinous smell. During the process it is necessary to agitate the mass throughout once or twice a day, in order to equalise the fermentation as much as possible.

As soon as the fermentation is considered to have progressed far enough the supernatant liquor is drawn off and fresh water run in, the whole well stirred up, allowed to settle, and the surface liquor drawn off. This washing is repeated as long as any perceptible colour is imparted to the water; after the last deposition and decantation, the starch will be found to have settled down in layers of varying purity, the topmost one containing the most gluten and albumen. These different layers are now taken up with a wooden shovel, and transferred to separate cisterns, where they are agitated with water and then passed through fine sieves. After the starch has again settled down, the clean water is drawn off, any impurity that may be on the top separated, and set aside to be washed up with the next batch; the underlying portion agitated again with fresh water, and purified by settling and decantation, this being repeated as often as may be deemed necessary.

It is then shovelled into wooden boxes about 4 feet long, 12 inches broad, and 6 inches deep, perforated throughout and lined with thin canvas; this is termed 'boxing.' When it has drained and dried into a compact mass, it is turned out by inverting the box upon a clean table where it is cut up into pieces 4 or 5 inches square; these are then set upon half-burned bricks, which by nature of their porosity absorb the moisture from the starch, so that the under surface of the blocks may not become hard and horny.

When sufficiently dried upon these bricks, the blocks of starch are put into a stove and left there until tolerably dry; they are then removed to a table, where all the sides are carefully scraped with a knife, next packed up in the paper in which they are sold, returned to the stove, and subjected to a gentle heat for some days, previous to being sent into the market.

II. Martin's process. In this process flour is employed in preference to the whole or crushed grain. It is kneaded into stiff dough with water, exactly as for bread-making, and allowed to remain in that state until every part becomes thoroughly saturated with moisture. This requires 25 minutes in summer and about an hour in winter. For the separation of the starch from the gluten an apparatus is employed,

consisting of two troughs, which are similar to each other, and which may be of any convenient length. Within each of these troughs there is a rectangular frame, which is caused to move to and fro within the trough by a crank axis and connecting rod, the crank of one trough being set opposite to that of the other.

Each of the frames carries the bearings of four or other convenient number of grooved rollers. At the bottom of each of the troughs there are openings at intervals covered with wire gauze; at the ends of each trough are applied spring buffing apparatus. Below the troughs is an inclined sieve of fine wire gauze, and below it an inclined shoot, down which the fluid which passes the sieve flows, and from it into any suitable receiving vessel, where the starch is allowed to settle; above each trough there is a perforated pipe, through which the numerous jets of water flow on to the dough introduced into the trough, and which serves to wash away the starch from the gluten.

The dough which is to have the starch separated from the gluten is formed into small balls, and placed in the troughs between the rollers. The frame carrying the rollers is caused to reciprocate, a constant spray of water being allowed to flow over the dough at the same time, by which means the starch is washed out and separated from the gluten; the milky liquor flows through the openings in the bottom of the trough on to the inclined sieve, and thence by means of the shoot to a suitable receiving vessel. Should any particles of gluten pass through the openings, they pass along the inclined sieve, and are received in a vessel. After the dough has been subjected for a sufficient length of time to the action of the rollers, it consists for the most part of gluten, and is placed between the ends of the frames and the buffing apparatus, where it is beaten for several minutes, and can then be used for any purpose to which it is applicable.

The purification of the starch obtained in this way may be effected in the usual manner, by successive washings and decantations as in the fermentation process, or by the inclined plane method described below under potato starch. Subsequently, Martin introduced the following process for the purification of the crude starch, whereby a better product is obtained than is possible by mere washing with water. This consists in treating the impure starch with a weak solution of sodium hydroxide, sp.gr. 1.013, in sufficient quantity to turn red litmus paper blue, after the deposit has been well roused up. The mass is then allowed to stand for two hours, during which time the gluten swells up, and becomes partly dissolved. A considerable quantity of water is then added, and the whole thrown on to a No. 200 sieve, which retains the swollen gluten and allows the starch to pass through; the starch is then run on to the inclined plane as before. Almost the whole of the starch is by this means obtained as a first product, whilst with simple washing about 25 p.c. is produced in an impure, unmarketable form.

On the average there is obtained from a sack of flour about 110 lbs. of moist gluten and about 220 lbs. of dry starch.

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According to Goldbeck (Chem. Zeit. 1916, 40, 829), modern methods enable larger yields to be obtained, the separation of the starch from the gluten being more perfect. Use is made of centrifugals to separate the starch from the sieved liquors, and the starch still retained on the sieves is freed from the admixed gluten by treatment of the mixture with dilute ammonia, and acetic acid, and centrifuging.

Traquair (J. Soc. Chem. Ind. 1912, 1016) mentions two plants in North Ireland for the production of wheat starch, their existence there being associated with the use of this starch as the finish for fine linen. The recovery of gluten is a feature of modern processes, an important outlet existing for it in the manufacture of diabetic foods.

20. *Manufacture of starch from potatoes.*—At one time the manufacture of starch from potatoes was carried on to a certain extent in Great Britain as well as in Ireland, the first published specification relating to starch being taken out as far back as the year 1717 by Newton, Nowell, Clark, and Joynes, for 'a way or method to make starch of and from the roots called by the name of potatoes,' but its development has been considerably checked by the potato disease, and is now entirely replaced by starch from rice.

In France, Germany and Holland however, where much more attention has been directed to the growth of the potato as a starch-producer, the manufacture of fecula or starch from this source has attained very considerable dimensions and large quantities of potato starch are exported yearly from those countries.

On the Continent the manufacture of potato starch, for an account of which the writer is much indebted to Payen's *Chimie Industrielle*, includes the following operations—steeping, washing, separation of stones, rasping, straining, settling, removal of the starch, purification, second straining, washing, draining, and drying in the air or in a centrifugal machine, drying in an oven, packing.

Steeping.—Potatoes which are grown in tough clay or loam are covered with adherent earth, which clings so tenaciously to them as not to be removed by simple washing; they are therefore allowed to soak for several hours in a large vat containing water.

Washing.—In France this operation is carried on as follows: An apparatus called the washing drum (Fig. 4) is used, consisting of a hollow

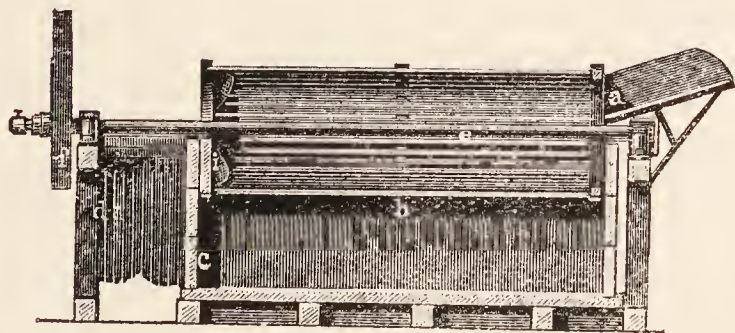


FIG. 4.

revolving cylinder *b*, formed of wood or iron bands, $\frac{1}{2}$ – $1\frac{1}{2}$ inches wide, and laid longitudinally from one end to the other, the distance between each being about $\frac{3}{4}$ inch, so as to allow of the escape of the dirt, sand, and stones, whilst the tubers are retained. The cylinder, which is slightly inclined, is immersed to half its diameter

in water in the trough *c*, wherein it revolves at the rate of about fifteen revolutions per minute, and by which means the potatoes are kept in continual motion, rubbing against and being rubbed by the sides of the cylinder. From the sides of the trough spring the boards *g*, slanting to the upper part of the cylinder, so as to prevent

splashing of the water. The cylinder is worked by a band from the main shaft, passing over the wheel *f*. The potatoes are fed into the hopper at *a*, and are thrown out at the opposite end, where, falling down the inclined plane *d*, they are conducted to the stone catcher (Fig. 5). This apparatus consists of a semi-cylindrical

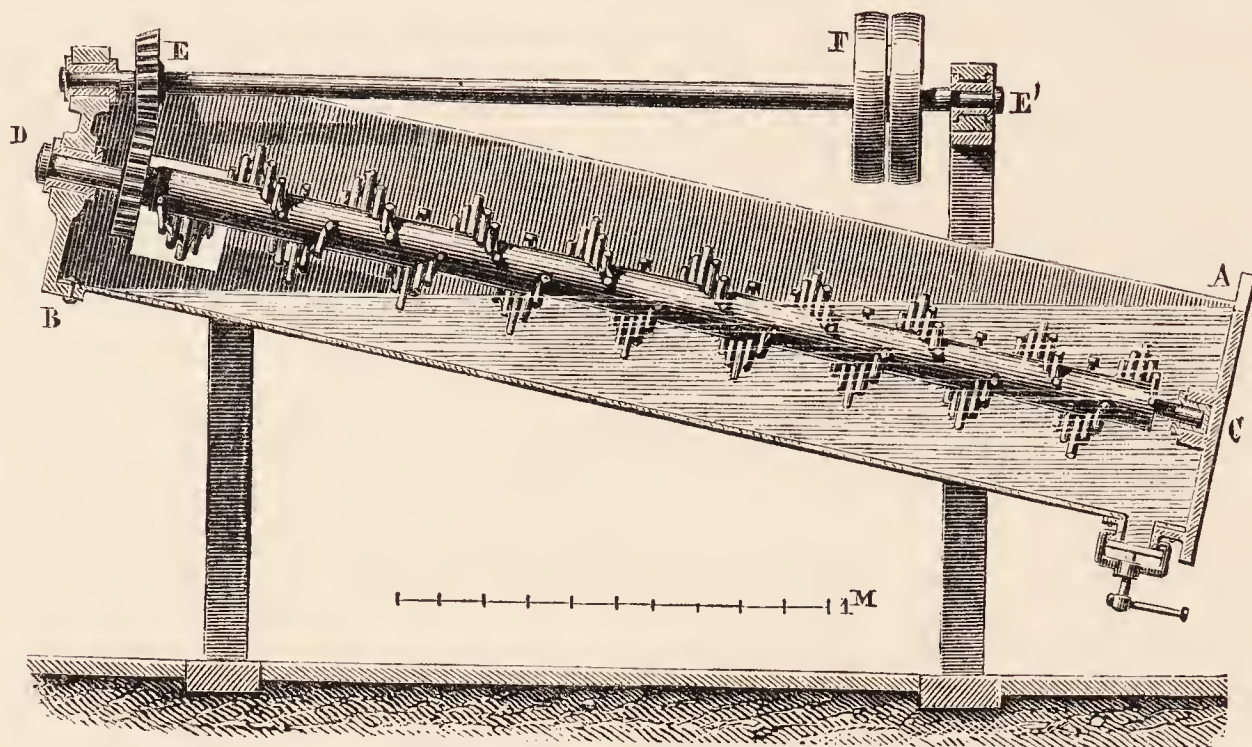


FIG. 5.

sloping trough, filled with water to the level *A*. In the trough is a shaft *D*, furnished with arms placed spirally (Figs. 6 and 7), and which by means of the cogwheel *E* is rotated by the driving

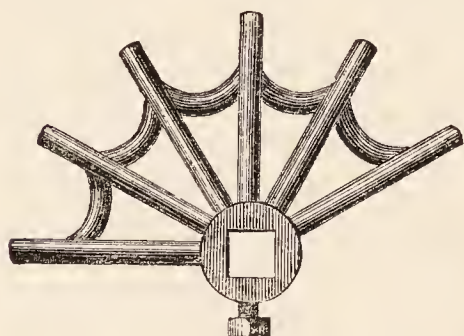


FIG. 6.

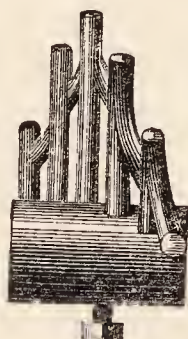


FIG. 7.

wheel *F*. The potatoes being fed in at *A*, are rubbed upon one another by the arms and repeatedly dipped in the water, so that the remainder of the dirt and all stones and sand are

washed off, and, the heavier particles sinking to the bottom, are removed from time to time through the opening *c*. The potatoes are carried forward by the action of the spiral until they reach the upper end of the trough, over which they fall into the hopper of the rasping machine.

In the German factories the above operations are carried on at one and the same time, the trough in which the washing drum is placed being divided into two unequal parts, the larger one *d* for the washing drum, and the other *e* for the stone catcher; as shown in Figs. 8 and 9, the potatoes are introduced into the smaller division *e*, and are drawn forward and kept in incessant motion by six or eight large iron arms *gg*, arranged spirally on a prolongation of the shaft of the washing drum *ab*. The stones, sand, &c., are drawn off at intervals through the openings *i* and *h*. The potatoes thus reach the

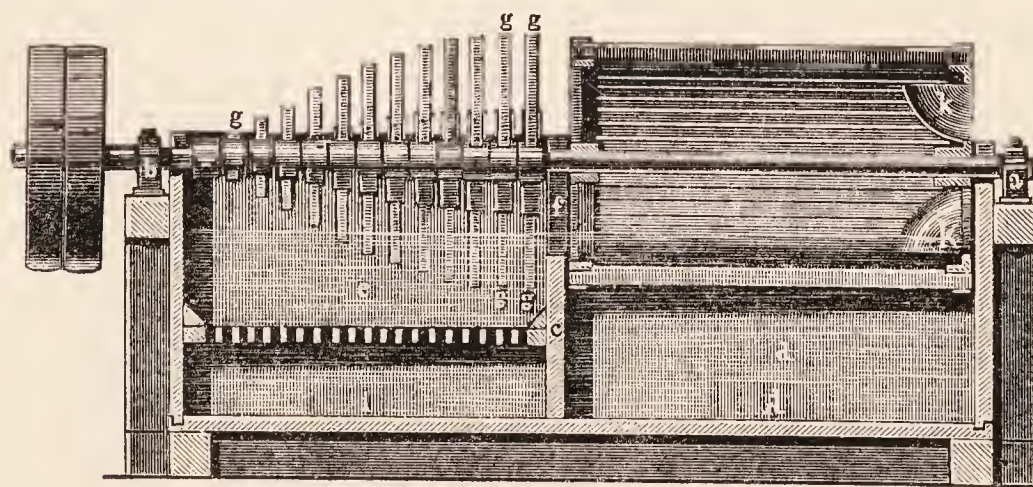


FIG. 8.

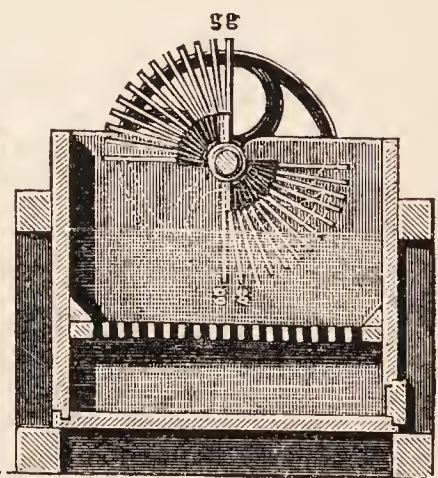


FIG. 9.

washing drum previously washed and freed from stones, from which they pass through *kk* to the rasping machine.

By means of this the tubers are reduced to a pulp, and the cells containing the starch

are ruptured; and the more completely this is done the greater the amount of starch obtained, since it is only the starch from the cells which are actually ruptured that can be extracted, whilst all that remains in closed

cells represents so much loss to the manufacturer. For this purpose Champonnois' rasper is generally considered the best, and is shown in Figs. 10 and 11. It consists of a hollow cylinder furnished with saw blades on its inner surface, against which the potatoes are made to rub. The case A of the cylinder is seen in Fig. 11, with the rasper inside. This is so arranged that from one to four saw blades lie between thin steel bands, at an interval of from $\frac{1}{50}$ to $\frac{1}{25}$ of an inch apart, and between each group is a space through which the pulp as it is formed can pass. This arrangement is shown in Figs. 12 and 13. In the axis of the rasping cylinder is a shaft BB, making 800 to 1,000 revolutions per minute, by

means of a band from the main shaft applied to the driving-wheels EE, and regulated by a fly-wheel. At the other end of the shaft, within the drum, is a strong fork-shaped scoop. The potatoes, falling through a side opening, are seized by the scoop, and pressed forcibly against the saw blades CC in the cylinder. Water, being admitted into the interior, is driven by centrifugal force against the sides of the cylinder, and makes its way through the interstices, carrying with it the potato pulp, which passes away through a pipe underneath. The teeth of the saw blades are very short, projecting one-fifth of an inch from the drum. They require reversing twice a day, and after two days' use need to be

FIG. 10.

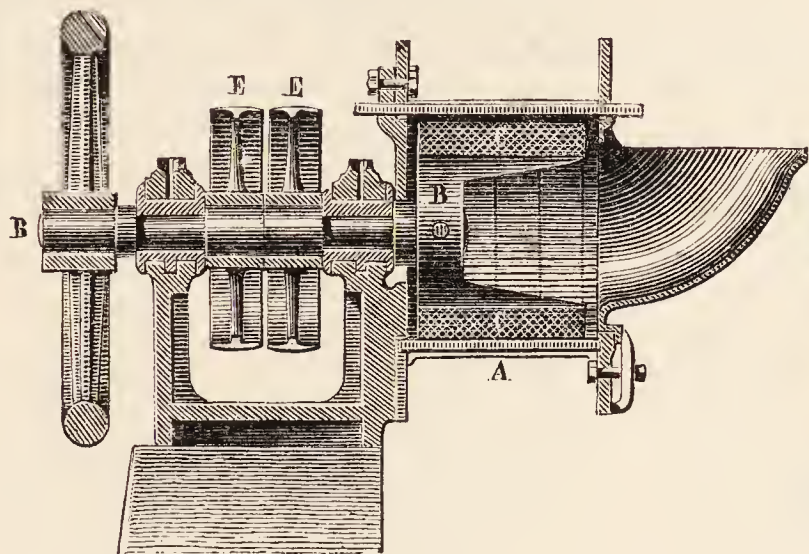


FIG. 11.

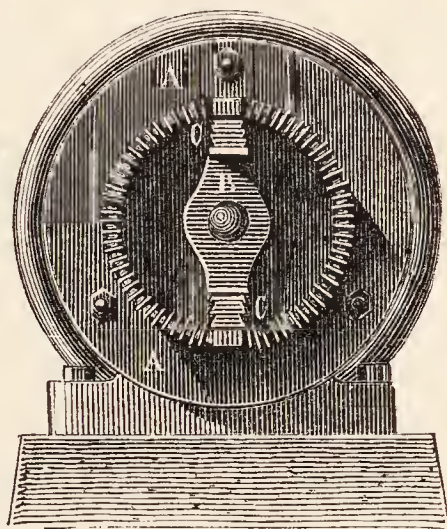


FIG. 12.

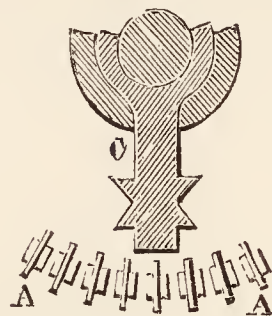


FIG. 13.

re-filed. As much as thirteen tons of potatoes can be rasped by this machine in ten working hours, whilst the yield of starch from a given quantity of potatoes is considerably increased.

The pulp thus obtained is a mixture of starch and fibre. In order to separate one from the other the pulp is washed with water upon brass-wire sieves of different degrees of fineness, which allow the starch granules to pass through with the liquid and retain the coarser portions of the fibre. Several forms of apparatus have been devised for this purpose, the principal objects aimed at being uninterrupted working, as complete exhaustion as possible of the pulp within the smallest space, and economy of wash water. Fig. 14 shows a longitudinal section of Huck and Stoltz's machine. This consists of three cylinders A, B, C, of different diameters. The case of the first is formed of a wire sieve, 25 meshes to the inch. The pulp from the rasper is run in through the funnel *a*. Within this cylinder is another, *bb*, formed of perforated metal plate into which water flows through the pipe *a''*, and is distributed uniformly upon the potato pulp in A by means of the perforations in *bb* from A. After parting with the greater part of its starch

the pulp is gradually brought forward into the second cylinder B, which is covered with sheet copper. The pulp is here worked about with a T-shaped iron fastened to the shaft DD', which is rotated by the driving wheel G in an opposite direction to the cylinder; from here it is carried forward to the third cylinder, which is covered with wire tissue, 35 meshes to the inch, where it meets with a fresh spray of water coming through the perforated pipe *dd* from *a'''*. Whilst in the cylinders A and C the pulp undergoes a continual working with brushes, which, like the agitator in B, are connected with the shaft DD'. These three cylinders revolve at the rate of 22 revolutions per minute; whilst the agitator in B makes 35 in the same time. The starchy liquid flowing from A and C is collected in the trough K, and runs from thence into the sieve cylinder HH', which is covered with wire gauze, 50 meshes to the inch. Here any fibrous pulp which may have passed through the other sieves is retained; whilst the water containing the separated starch is run off along the trough L into the settling vats. The coarse pulp as it is pushed out of the cylinders falls into the receivers MM' underneath. In order to prevent the clogging of the sieves, a fine stream of water

is thrown upon them during working from pipes running parallel with their axis.

A modification of the above apparatus, by means of which considerably less water is required, and which is suitable for localities where water is more or less scarce, is shown in Fig. 15.

The pulp coming from the rasper A is raised

by means of a centrifugal pump into the first cylinder B, where it gives up by far the greater part of its starch. The strained liquor from this cylinder is not joined with that from the other cylinders, but runs straight away into the purification vessel. The liquor from the mixing cylinder C and the other sieve cylinder D, con-

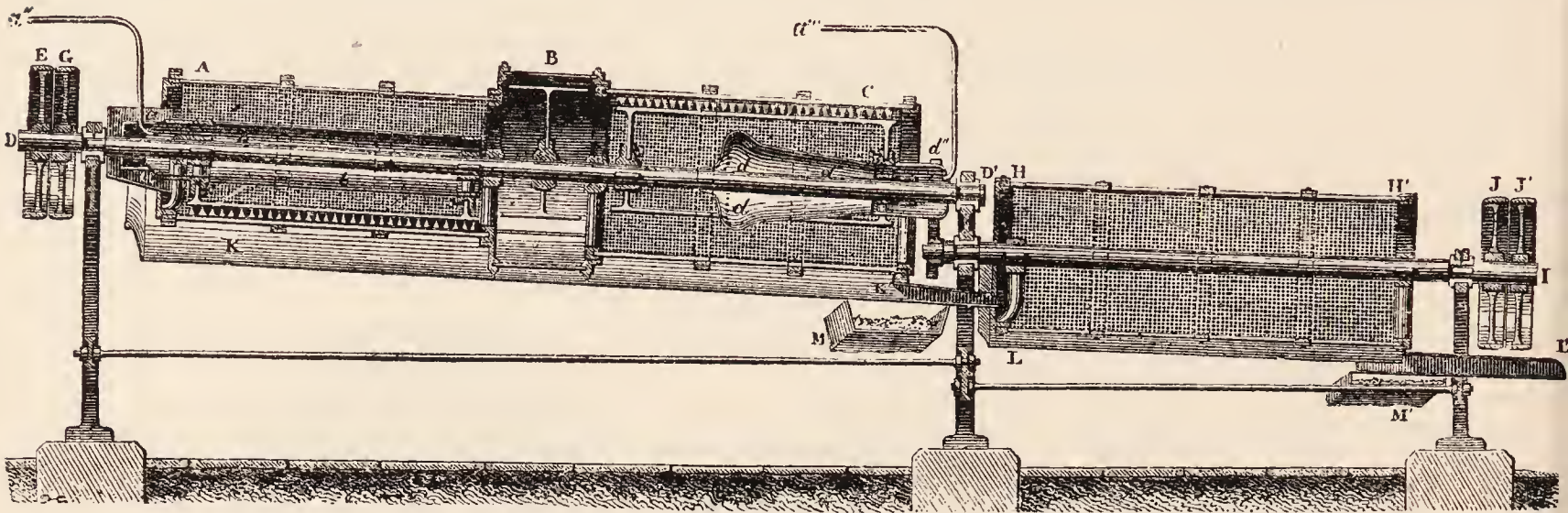


FIG. 14.

taining comparatively but little starch, is carried by the pipe GG' back to the rasper, where it is used instead of clean water for the thinning of the pulp.

In some factories, by means of a modification of the apparatus just described, a second working of the pulp is effected, and a larger yield of starch thereby obtained. This is shown in Fig. 16. The pulp, thinned with water, falls from the rasper A into a small cistern, from which it is raised by the pump B, through the

pipe B', into the sieve and mixing cylinders D, D', D'', and in the latter washed by a stream of water a'. The pulp rejected from D'' falls into the hopper of a second rasper, where it is rubbed between two cylinders F rotating in opposite directions; from thence it flows into the sieve G, where it meets with more water from a'', and, being washed, falls into a trough, along which it is pushed by an Archimedean screw.

The starchy liquid from D falls into the trough E, that from G into E', and both united

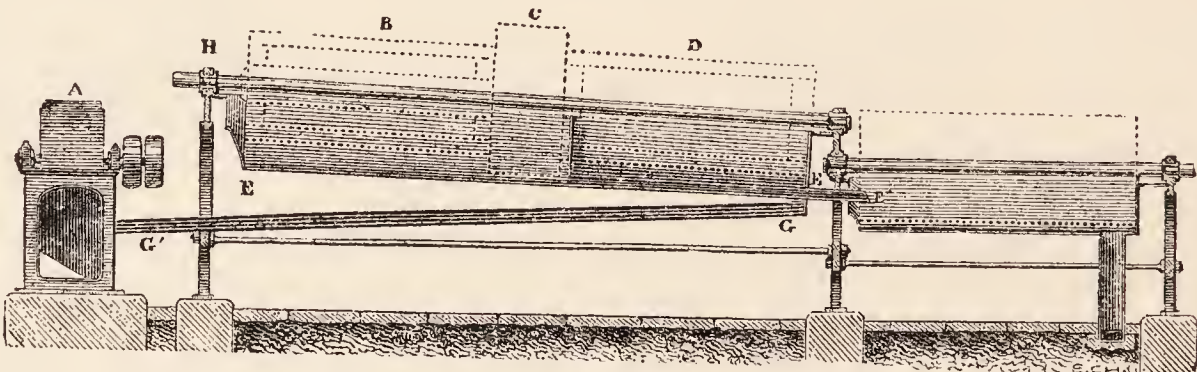


FIG. 15.

fall into the first purifier KL, thence into the trough J, into the cistern M, from whence it is raised by the pump to the second purifier O, where the last portions of fibre remain, whence by means of the trough P the liquor containing the nearly pure starch passes to the purification apparatus. In the smaller factories this is generally accomplished by means of settling vats.

In addition to rasping, many manufacturers are accustomed of late years to grind the pulp after rasping, whereby a slightly increased yield of starch is obtained. The following figures, calculated on the starch worked, show a comparison between the yield obtained when a rasping machine only is employed, and when, in addition thereto, grinding is carried on as well.

Obtained in form of green starch	Without grinding	With grinding
Experiment A. . .	81·8	87·4
Experiment B. . .	76·3	85·5

Various forms of machines for carrying on the rasping and grating processes simultaneously have been constructed during the last few years.

The starchy liquor as it comes from the sieves generally contains some sand, which was not separated during the washing of the potatoes, and was too fine to be retained by the sieves. It is therefore run into a large vat and vigorously stirred so as to bring all the starch into suspension, and, before it has had time to settle, is siphoned off into another large vat, where it is allowed to stand for four hours, during which time the starch settles on the bottom. The sand, by reason of its greater specific gravity, sinks rapidly to the bottom, and remains in the first vat. The lower part of the sediment deposited in the second vat consists of pure starch, covered by a greyish layer, consisting of fine fibres that have passed through the sieves. The supernatant liquor having been run off, this

impure mass is scraped off as clean as possible with an iron scraper. This impure starch is agitated with fresh water, passed through a very fine sieve, and allowed to rest for some time, until a further amount of white starch falls out, when the same operation is repeated.

and of sufficient consistence, divided into lumps and placed to dry.

Sometimes the starch, deprived of its supernatant brownish deposit, is purified by being placed in a slightly sloping flat-sided trough about 22 feet long and 3 feet wide. Below this is a second trough, inclined in the opposite direction; and below this a third, inclined like the first. A spray of water from a very fine rose falls upon the starch, which is placed just beneath it at the top end of trough No. 1, and at the same time is kept constantly stirred. The water gradually washes everything forward with it, and while slowly flowing along the troughs the starch is gradually deposited; whilst the lighter fibrous matter remains in suspension, and passes with very little starch into vats underneath. The starch obtained in this way is added to that purified in the first settling vat, and is then ready for draining.

In large factories the settling vats have been entirely superseded by the inclined plane; this consists of a series of three wooden troughs, Fig. 17, $3\frac{1}{2}$ feet wide and about 30 yards long, each having a fall of 1 to $1\frac{1}{2}$ in 1,000. The third plane or trough rests on the ground and empties into the vat G. The second and first are affixed to wooden supports as shown. The starchy liquor, as it comes from the cylinder sieves, enters the first inclined plane at A, flows along in the direction AB, and thence along CD to F. the flow being regulated at will by means of the screw valves at B and D. The greater part of the starch is deposited in the first plane, from which it is removed once a day. The starch from the second plane, on which considerably less is deposited, is removed twice a week; and that from the third once a week. The liquor, containing very little starch, flows into vat G, or generally into a series of vats, whereby any starch that may still remain in the wash water is collected.

The starch thus deposited on these inclined planes is sufficiently pure for most purposes to be sent at once to market; but, as it is still contaminated to a slight extent with potato sap, it is advisable to wash it once or more in the usual settling vat in order to purify it completely.

Drying.—The starch is taken from the planes or settling vats in the form of a very thick mud or sludge, from which the greater portion of the water may be removed by centrifugal action, by drying in the air, or in ovens.

In the drying of starch by centrifugal action the same form of apparatus is used as in the manufacture of sugar, but as the starch mud is so thick as to render it incapable of being properly distributed on the sides of the machine, a quantity of water is mixed up with it to bring it into a sufficiently thin paste that will flow into the apparatus whilst it is in motion. It is then flung against the circumference of the machine, the water flies off, and the starch lies as a compact mass round the sides of the cylinder. Advantage has been taken of centrifugal action for the purification, as well as for the drying of starch at the same time, by Fesca, of Berlin. When the impure starch liquor is introduced into the machine, the densest and heaviest portion—and consequently the purest starch—is driven first against the sides of the cylinder. The fibrous portion remains longer suspended,

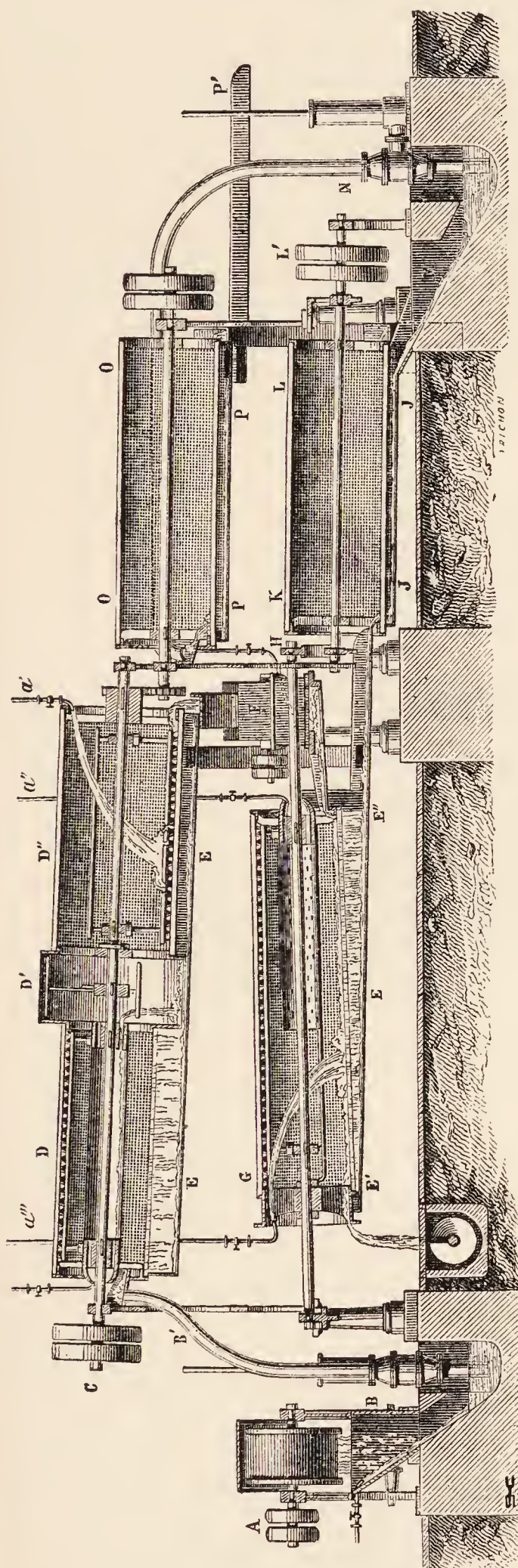


Fig. 16.

The purified starch is again agitated with water, passed through a silk or wire sieve, 90 meshes to the inch, and again allowed to settle, the liquor decanted off, the surface of the starch scraped, and finally, if the mass be pure enough

and is deposited as a layer upon the surface of the pure starch, from which it is easily removed.

For many purposes—such as the manufacture of dextrin and glucose, &c.—the starch, as it comes from the centrifugal machine, and containing from 35 to 40 p.c. of water, needs no further desiccation, and is known in commerce as green starch.

In factories where a centrifugal machine is not used, the water is removed as much as possible from the starch before proceeding with the drying. Accordingly, as soon as the starch is considered sufficiently purified, it is dug out of the settling vats and transferred to perforated boxes, lined with clean linen, and set aside for some time to drain, during which time it acquires sufficient hardness to enable it to retain the shape of the box, and as soon as ever this takes place the box is inverted upon a dry porous slab, generally of plaster-of-Paris, which abstracts a

further amount of moisture, so that it arrives at the state of green starch. It is now sufficiently solid to be removed to the drying room, on either side of which a series of shelves, formed of bars of wood placed at a distance of about one inch apart, are ranged in tiers one above the other, through which a current of air is made to pass freely by means of louver boards or venetian ventilators. On these shelves the blocks of starch are placed, and allowed to remain for six or eight weeks, until sufficiently dried. One great drawback to this method is the exposure of the starch to any dust that may be floating about in dry weather, as well as the possibility of the moist starch becoming frozen in cold weather. The latter may be obviated by introducing heated air into the drying-room, and the dust precluded by shutting up all the windows—in fact, by practically converting the room into an oven. The starch dried in this manner is known as 'hurdle starch.'

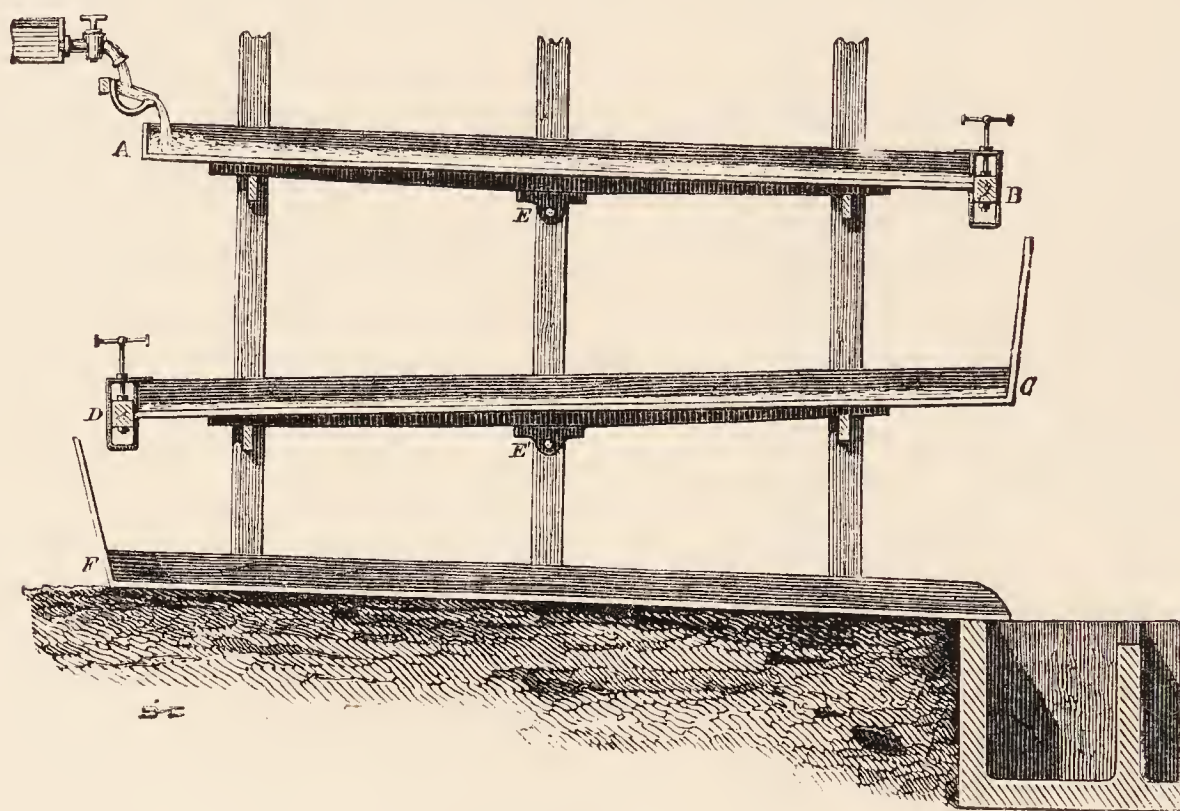


FIG. 17.

The best quality, termed superior, which is used for the manufacture of starch sugar and dextrin, is singularly white, glossy and pure, and consists of large grains, being the first to deposit in the settling tanks. The deposits become lower in quality in succession. The gloss of starch depends on the size of the grain, the larger the grains the better the gloss, and the determination of the diameter of the grains by means of the microscope forms a good test for this starch.

A superior article consists of grains having a diameter 35.5μ , ordinary prima 32.5μ , prima seconds 21.0μ , and inferior kinds 17μ to 12.5μ . Considerable importance is also attached to the amount of impurity present, such as coal dust, potato skin, soot, sand, iron particles from wheels, algæ from water, particles of wood, &c. The amount is ascertained by smoothing a sample on white paper, and counting the particles in a square cm. Superior starch contains 15 to 30 particles, average samples 27–170, while inferior kinds contain as many as 800 upon 1 sq. cm.

RICE STARCH.

21. *Manufacture of starch from rice.*—Although it had long been known that rice contained more starch than any other starchy material, the difficulties of manufacture were so great that the industry was not established until about 1860.

It will be seen that the production of starch from potato, wheat, maize, &c., is very largely a mechanical process, but in the case of rice, the structure of the grain is such that so far mechanical separation of the starch from the albuminoids, &c., has not been successful. Serious attempts have been made, however (see Eng. Pat. 147255, 1919, Hardy and Reckitt).

In order to prepare a commercially pure rice starch, chemical treatment of the grain is necessary, and advantage is taken of the solubility of the rice albuminoids in dilute caustic soda.

The demand for rice starch has grown chiefly because of its suitability for laundry use,

and this in turn is due entirely to the fact that the rice starch granule is considerably smaller than that of any other commercial starch. When made with boiling water, too, the resulting mucilage is better adapted for 'starching' than other starches.

The raw material for the rice starch industry is cleaned broken rice (grain from which the husk, &c., and germ have been removed), produced in the process of preparing whole or partially whole rice for culinary use.

At one time the sole source of supply was India (Bengal or Madras), but during recent years supplies have been drawn from Burma, Siam, and Saigon.

Almost any variety of broken rice is suitable for starch manufacture, provided it is not too small; otherwise there would be great waste in the softening process. It should be reasonably free from adhering dust, and uncleaned skin or husk. It is purchased upon appearance, and not upon analysis, and each year the Eastern Rice Millers furnish the Rice Brokers with 'type samples,' of the various grades for the current year.

ANALYSIS OF BROKEN RICE.

	Burma	Siam	Saigon	Whole rice, including husk
Water . . .	12.0	12.0	12.0	12.5
Albuminoids . .	7.0	7.8	7.5	6.3
Ash . . .	1.0	0.8	0.8	5.9
Fibre . . .	0.5	0.5	0.5	8.0
Sugar and Gum	0.5	0.4	0.4	0.3
Fat . . .	0.5	0.5	0.5	2.1
Starch . . .	78.5	78.0	78.3	64.9
	100.0	100.0	100.0	100.0

Process of manufacture.—The extraction of the pure starch from rice and its subsequent formation into starch crystals may be dealt with for simplicity under the following heads: (1) steeping, (2) grinding, (3) separation of starch granules from the fibre and gluten liquors, (4) moulding and drying.

1. *Steeping.*—Great importance is attached to the first stage in this process. It is not simply a question of softening the grain preparatory to the subsequent grinding, but a chemical treatment, in which weak caustic soda (decinormal strength) is used. The caustic alkali dissolves from one-fourth to one-third of the albuminous substances which cements the starch cells together, the removal rendering them more amenable to the after treatment.

The rice is first gently washed with water to remove dust as it travels along a worm conveyor into a series of shallow steeping frames. These are made of reinforced concrete or wood, and are fitted with perforated tiles to allow the steeping liquors being drawn off when exhausted.

The frames are filled with the washed rice to the depth of 10 ins. to 12 ins.

A weak solution of caustic alkali is sprayed over the surface of the rice until the latter is well covered with the steeping liquor. After soaking for a time the liquor is drained off, the rice turned, and the process repeated with

fresh alkali a number of times until the rice is thoroughly softened and ready for grinding.

Steeping in this manner with, say, four washes takes 12 to 14 hours. The alkali steeping liquors must not be too strong, otherwise the starch granules swell, and the subsequent separation is extremely difficult.

2. *Grinding.*—The steeped rice when thoroughly drained is ground between mill-stones. The feed to these stones is most carefully regulated to ensure complete grinding. Incomplete grinding must be avoided as much as possible on account of the loss in starch yield, and therefore in some factories the rice is passed through two mills arranged side by side, so that the ground starch drops directly from the first into the second mill. Grinding is facilitated by the addition of weak alkali or water to the rice as it is fed under the stones. The ground rice should leave little or no residue on an 80-mesh sieve.

3. *Separation of starch from the ground rice and liquor.*—The rice paste as it comes from the grinding is too thick to admit of the direct separation of the starch, and must be further diluted with water and alkali; additions of the latter are made to dissolve more of the albuminoids, and prevent fermentation. There are two methods for separation of the starch most commonly used; these are:

(a) The macerator process.

(b) By centrifugal treatment and sieving.

(a) *The macerator process.*—The rice paste is run into wooden or concrete tanks (vats) fitted with stirrers. These tanks are about 10 ft. square, and 6 ft. to 7 ft. in height. A certain proportion of the ground paste is run into each tank, so that when filled up with water and stirred the density of the liquid is from 2°–3°Tw.

After a short time the stirring is stopped.

Owing to the fact that the fibre settles much more quickly than the starch, the top starch liquor can be drawn off from the fibre. The macerators are fitted with observation glasses and plugs. By these means a clean separation is quite easy. The starch liquor drawn off in this way is settled on large frames for 36 hours. In this time the starch completely settles out and can be dug off, while the supernatant liquor is discarded. The fibre left after the top starch liquor has been removed is re-washed with more water, and the process repeated. By this means all the available starch can be extracted, and the final residue of fibre and any unground rice is pressed for cattle food.

(b) *The centrifugal and sieving process.*—The rice paste from the stones is diluted with water and alkali, to about 18°–20°Tw. (22 p.c. to 24 p.c. solids).

The starch is separated from this dilute liquor by spinning in centrifugal machines. As the machine is set spinning the liquid is fed into it until full (70 to 80 gallons). The speed of the machine should not be less than 700 revolutions per minute.

As the spinning continues the heavier particles of unground rice and starch are spun out to the back of the machine, while the lighter particles, such as fibre, with which is entangled a small quantity of starch, are spun out last on the surface of the starch. When the machine

is stopped this soft slimy deposit on the starch surface is scraped off, and together with the liquor is collected and treated to extract by the macerator process described above all the available starch.

The starch deposit, between $1\frac{1}{2}$ ins. and 2 ins. in thickness, is dug out of the machines into pug mills, where it is mixed with water and reduced to 20° – 22° Tw. ready for sieving.

It is necessary to sieve the starch 'milk' at this stage to remove any unground rice deposit spun out with the starch, and also the coarse fibrous matter, which it is impossible to remove by scraping.

Rotating cylindrical sieves are almost invariably used for this purpose, and are constructed as follows :

A shaft 4 to 5 yards in length is provided at regular intervals with a number of rods of equal length arranged symmetrically at right angles to the shaft. The ends of these rods carry six wooden boards parallel to the shaft. The frame-work thus formed is covered with the finest silk gauze. The cylinder is so arranged that one end of it lies a little higher than the other.

The starch liquid to be strained is fed into the upper part of the apparatus. The starchy liquor as it filters through is collected in a wooden or zinc casing which completely surrounds the cylinder, whilst the coarse tailings remaining in the sieve pass along, and are collected in a special trough at the lower end of the cylinder.

The coarse tailings are diluted with water, and all available starch extracted by either the macerator process, or further sieving and spinning. The starch liquor which has filtered through the sieve is re-spun to separate the starch, and to remove more and more of the contaminating gluten liquor.

The starch separated in the second spinning operation is dug out of the machine and reduced to a liquid of 36° Tw. by the addition of water and alkali. The addition of alkali to the starch prevents fermentation during the subsequent process. The thick starch liquid so obtained is run into 'exhausts' where a large amount of water is removed by means of a suction pump, leaving the starch in a solid form convenient for handling.

4. *Moulding and drying starch.* (a) *Moulding the starch.*—The starch which is dug out of the exhausts contains too much water to allow of cutting up into blocks. It is filled into perforated wooden boxes in which is a piece of filter cloth. These boxes are then shaken by means of a mechanical 'knocker,' which enables the starch to take the shape of the box.

These boxes are then put into hydraulic presses which squeeze out an appreciable amount of water through the perforations. The pressure should not be more than three-quarters of a ton per square inch, otherwise the pressed starch becomes cracked.

After pressing, the boxes are emptied and the starch is then in one solid piece ready for cutting up into blocks for drying. Each length of starch is cut up by a circular saw into a number of cubes about 6 ins. to 7 ins. each side.

(b) *Drying the starch.*—The cubes referred to above contain 40 to 45 p.c. water, and are

first partially dried in 'crusting stoves.' These stoves are heated by circulating hot water under pressure through a series of pipes. The maximum temperature in the stove is 160° F. The blocks of starch are put on wooden laths which are placed immediately upon the hot pipes. The time for this preliminary drying is from 14 to 18 hours, according to whether the stove is lightly or heavily filled. When dried in this way a thin crust is formed on the starch, which is slightly discoloured. This crust is scraped off and re-treated and washed and mixed with subsequent makings.

The remaining starch may now be completely dried without any further development of the yellow colour taking place. All attempts hitherto to avoid this crust formation have failed, although the extent of discoloration can be largely controlled. The crust constitutes about 20 or 30 p.c. of the total starch.

Large masses of starch when dried fall into more or less irregular shaped, rod-like pieces, so-called 'crystals,' the size, shape and smoothness of the surface of which depends greatly on the rapidity of drying and the solidity of the block before drying. Too rapid drying causes the starch 'crystals' to be small, while the presence of fibre makes them rough and 'crinkly.'

The cubes, after the preliminary drying and removal of the yellow crust, contain from 25 to 28 p.c. water. They are then wrapped up in paper, carefully tied, and placed on racks in large drying stoves containing from 4000 to 7000 pieces. Each piece is isolated to allow of a free current of hot air. The drying stoves are well ventilated, and are heated by steam radiators which can be carefully regulated. For the first few days the stove temperature is from 70° – 80° F. The temperature is then steadily and more rapidly raised up to 110° – 120° F. The drying operation takes about three weeks. Starch dried at too high a temperature during the earlier stages loses its colour and brightness, and may become quite yellow. When taken from the stoves the starch contains 10 p.c. of moisture, and the starch 'crystals' are completely formed.

As the starch at this stage is rather too dry and brittle, it is allowed to absorb moisture up to 15 p.c., which is the commercially recognised standard.

For this purpose the starch blocks wrapped in the original paper are placed in a damp chamber on racks similar to those in the stove. The atmosphere in this chamber is kept moist by means of a continually wet floor, or saturated bagging. After from 3 to 4 weeks the starch will have taken up the required extra moisture.

In both the operations, drying and subsequent absorbing of moisture, the quality of the paper used to wrap the starch has an important influence. It should be reasonably porous.

Method of quick drying.—Some such method as described above for drying the starch is necessary when starch 'crystals' are required. When the final starch is to be powder in form, much time and expense can be saved by drying in the following way :

The starch before it is re-spun in the centrifugal (as explained above) is adjusted to the right alkali test. After spinning, it is dug out of the machine, put through a cracker, and dried

on shallow trays. The trays are built up into stacks, one above another, 15 or 20 high. Each stack is placed on a truck, and when dry each truck-load will contain about 3 cwts. of starch.

The trucks of trays containing the wet starch are pushed on rails into a stove. The drying is effected by hot air, driven by a large fan. Each truck passes through the stove in from 36 to 48 hours. A constant supply of hot air is necessary, and the temperature of the ingoing air is maintained at 140°–150°F.

In the manufacture of starch every care must be taken to prevent fermentation starting at any stage in the process. The early removal of gluten liquors and care in preventing admixture with contaminating liquors are important. In the early stages the starch liquors are kept high in alkali, and in hot or thunder weather additional precautions are taken to prevent fermentation.

Waste products.—These consist of gluten and fibrous matter with which is entangled a certain amount of starch.

The fibre is pressed in filter presses, and finds a small market as cattle food

Rice gluten has not been prepared in a pure form on a commercial scale. Up to the present there has not been a sufficient demand. The alkaline liquors obtained in the process of starch manufactured from rice contain from 1 to 2 p.c. of gluten, which is recoverable.

The starch must be allowed to settle out from the gluten liquors, and from the clear liquors thus obtained the gluten is precipitated by the addition of acid or carbon dioxide, or by partial fermentation.

The method of rice starch manufacture described by Jones (Eng. Pat. 8488, 1840) is here inserted as being of historical interest.

One hundred pounds of rice are placed in a tinned copper or stoneware vessel holding 50 gallons of a solution of sodium or potassium hydroxide, containing 200 grains of alkali per gallon of water; the mixture is well stirred and allowed to macerate for 24 hours, at the end of which time the liquor is siphoned off and the rice well washed with twice as much cold water as there was of alkaline solution. The water is next poured off and the grain placed upon sieves to drain, after which it is crushed or ground to flour with rollers or millstones. The flour is then passed through sieves by means of brushes, the coarser particles which do not pass through being returned to the mill to be re-ground and again sifted, until the whole is thus disposed of.

The flour thus obtained is again treated with alkali solution, one hundred pounds of the rice flour being added in small quantities at a time to every hundred gallons of liquor. The whole is repeatedly stirred up during 24 hours, and then allowed to stand for about 70 hours, to settle. The processes of this deposit take place as follows: the first deposit consists of fibrous matters with little starch, followed by a deposit of the greater portion of the starch, the gluten and other matters remaining in solution in the alkaline liquor, which is siphoned off, and double as much water run on. The deposit is then well roused up with it, and the whole allowed to stand about an hour, during which time the matters other than starch subside, carrying with them a small portion of the starch, but leaving

by far the greater bulk of it suspended in the liquor. This is drawn off and passed through fine silk sieves. A further quantity of water is added to the deposit and agitated as before, and after standing a short time again drawn off and passed through sieves as before, this operation being repeated as often as necessary, until at length the whole of the starch is separated from the fibrous and other matters.

All these starchy liquors are then collected into one vessel, and allowed to settle for about 70 hours, during which time the whole of the starch is deposited. The supernatant liquor is now drawn off, and the starch (blued if necessary) drained, dried, and finished in the usual way.

Several other patents for preparing starch from rice have been taken out by various manufacturers, the principal of which are the following:

Berger's process (Eng. Pat. 9013, 1841). By this method:

1. Starch is manufactured from rice by the application of an alkaline salt, *e.g.* sodium carbonate, whereby the gluten is dissolved or freed, so that the starch may be separated therefrom. The operations are in all respects analogous to those of Jones' process.

2. The rice is soaked in water and submitted to a process of fermentation; or

3. The first and second processes are combined. Colman's process (Eng. Pat. 2166, 1841):

1. Rice is mixed with the refuse from wheat or other grain in the proportion of fifteen pounds of the latter to every hundredweight of rice, and, the necessary quantity of water being added, the mass is allowed to ferment for 10 to 15 days, after which the starch is separated by washing and sifting as already described.

2. The rice is steeped in water for 4 days, then drained, and reduced to a pulp in a mill under a stream of water, collected in a reservoir, allowed to settle, and the water siphoned off.

The deposit is then agitated with a dilute solution of hydrochloric acid (about 2 p.c.), and allowed to stand for 5 days, being well stirred every 4 hours during that time, then allowed to settle for 18 hours, the clear liquor drawn off, and the operation repeated with a 0.5 p.c. acid solution. Finally, the deposit is washed with large quantities of water, passed through sieves, drained and dried in the usual way.

Rehe patented a process (Eng. Pat. 10359, 1884), according to which the rice is first submitted to a temperature of 160°–180°F. before steeping, and afterwards macerated in soda lye (four pounds of soda to every hundredweight of rice), and the starch extracted in the usual manner later on.

Ransford introduced a process (Eng. Pat. 603, 1853), in which pressure is applied to the rice after it has undergone the steeping operation. The rice having been put into the steeping liquor, in a vessel capable of being closed down, is allowed to steep for some time. The vessel is then closed down tight and more liquor forced in by means of a pump, up to about 20 lbs. to the square inch; this is continued for a short time, the liquor drawn off, and again pumped in. The liquor is then drawn off, and the rice further pressed so as to drive out as much gluten as possible, after which it is ground and treated in the usual way.

In Germany the manufacture of starch from

rice has replaced wheaten starch to a large extent, and J. Berger, who appears to have given much attention to this subject, has published an interesting account of the process as carried out there at present (*Chem. Zeit.* 14, 1440, 1571; 15, 843).

22. *Maize Starch* (W. P. Kaufmann, M.D., C.M., *J. Soc. Chem. Ind.* 1910, 547).—The manufacture of starch and its products from maize, and the by-products which result therefrom, forms a large and actively growing industry in North America. A succinct general description of the processes by means of which the various proximate constituents of maize are separated from one another will perhaps be the best means of showing the characters of these products.

Steeping.—The dry grain from the granaries is conveyed into large hopper-bottomed steeping vats, and water impregnated with sulphur dioxide is run upon it. By means of steam syphons the water is kept in circulation, and at the same time heated and maintained at temperatures varying from 120° to 140°F. This steeping process is continued for from 2 to 4 days, according as the corn is more or less amenable to the softening and disintegrating influences, or is required to be less or more friable or 'soft' for the process to follow. The steep waters may be run to waste or may be evaporated for the recovery of the soluble material therein for the manufacture of cattle feed.

Milling.—The steeped corn is next run through Foos mills or their equivalent, by which means it is cracked, decorticated, and partially ground, giving rise to a diffuent mass. This, when appropriately diluted with water so that the most finely ground portions form a liquor (separator liquor), is passed through a germ separator—a long large V-shaped tank with a screw conveyor at its bottom and skimming paddles at the top. The oil-bearing germ floats and is skimmed off, and the endosperm starchy and glutinous matter, cortical tissues, bran, and fibre matter pass on. The germ is then conveyed away, washed free from adherent starch, and dried. The dried germ is next ground, 'cooked' with live steam, and its oil expressed by hydraulic presses.

The resulting products are:—

Corn oil—used largely in the manufacture of soap.

Oil cake (called 'maize germ cake' in England)—used as a cattle feed. Composition:—

Moisture	9.50
Protein	21.30
Fat	13.29
Carbohydrates	45.64
Fibre	8.27
Ash	2.00
		100.00

The cortical and endospermal portions, the most finely ground of which when suspended in water give rise, as already stated, to the 'separator liquor,' are next screened by passing them over a vibrating copper sieve. The coarse material separated is led into burr-stone mills with the necessary quantity of water, and is finely ground, the effluent from the burr-stones being combined with the previously separated 'separator liquor.' This mixture is then

pumped over the shakers. The first shakers are vibrating screens covered with silk bolting cloth of rather coarse mesh. By this means the starch 'liquor' is separated from the wet 'feed' or branny portions of the grain. This latter is conveyed into a stirring tub, agitated with water, and pumped over the second shakers, on which it is washed as free from starch as is possible.

The bran is next conveyed to presses where water is squeezed out of it, and it emanates therefrom as 'press feed,' an article much used in that state as a cattle feed. Or after being dried in appropriate apparatus it is bagged and sold as 'corn bran,' the average composition of which is:—

Moisture	8.93
Protein	10.50
Fat	2.75
Carbohydrates	65.04
Fibre (insoluble)	12.30
Ash	0.48
		100.00

The liquors separated from the shakers and mill are now combined and are known as the 'mill liquor,' or 'crude starch liquor.' They may be passed over another series of fine sieves or shakers to screen out the more or less gritty, glutinous and fibrous residues, or they may be passed immediately over the runs, trays, tables, or gutters, these terms being used synonymously.

The runs are gutters about 120 ft. long, 6 or 8 ins. deep, and may be from 10 ins. to 2 ft. wide, and above all, level, except for a drop of about 4 ins. between the ends. Into these the crude starch liquor is run and during its passage through them the starch, more or less free from gluten and cellular matter, is deposited, the glutinous and other residues 'tailing off,' carrying from 40 to 50 p.c. of starch, which, however, cannot be economically recovered as starch. The run tailings are conducted into 'continuous settling tanks,' where the solids are allowed to subside, while the clear supernatant liquid is syphoned off and run into the sewer.

The run tailings so concentrated are sold as a liquid feed under the name of 'slop' or 'swill,' or they may be pumped through filter presses, the solid material collected, dried, and sold as gluten meal, the average composition of which is:—

Moisture	9.74
Protein	31.20
Fat	2.35
Carbohydrates	54.67
Insoluble fibre	1.44
Ash	0.60
		100.00

This gluten meal is often mixed with certain proportions of corn bran while both are yet wet, the mixture dried and sold as 'gluten feed,' the average composition being:—

Mositure	5.78
Protein	22.80
Fat	1.99
Carbohydrates	62.10
Insoluble fibre	6.68
Ash	0.65
		100.00

Those who have made comparisons of the dietetic values of protein-containing cattle feeds have found great advantages in using those feeds obtained as by-products of maize. Professor F. T. Shutt, of the Dominion Government Experimental Farm at Ottawa, considers that maize protein is the most efficient source of nitrogenous food for cattle, swine, &c.

The 'green starch' (that which has been deposited on the 'runs'), instead of being utilised for the production of saccharine products, may be manufactured into different varieties of starch to meet various industrial and domestic requirements. This 'green starch' may be passed over the 'runs' a second time, the effect being that its gluten content is lowered from about 0.5 p.c. to 0.3 p.c., and according to the use for which it is destined, it may or may not receive a 'chemical' or 'alkali' treatment with caustic soda before re-running.

The varieties of maize starch which are found on the market may be classified as: (1) Thick boiling starches, (a) 'chemicalled,' (b) 'unchemicalled.' (2) Thin boiling starches—prepared by (a) the 'drying-in process,' (b) the 'in-suspension' process.

'*Chemicalled starches.*'—The effect of alkali, as used in 'chemicalling' starches, is to cause swelling and flocculation of the protein and fibrous matter, and saponification of the fatty impurities retained by the starch, and to induce these to 'tail off' and leave a purer and whiter starch when deposited a second time on the runs.

After passing over the runs, the starch, whether alkali or not, is shovelled into 'breakers' suspended in water to form a liquor of a gravity of about 22°Bé., and then pumped into cloth-lined perforated boxes—the moulding boxes—which are placed on the 'boxing horses.' By this means the water drains through the cloths, while the starch remains behind, and is subsequently 'broken out' into large cubes of 7 to 8 in. edge. At this stage the starch contains 44–45 p.c. of water. These cubes, after being broken out, are sometimes placed on porous bricks for a short time, water being abstracted from them, and causing them to 'set,' the starch then containing 42–43 p.c. of water. They are then removed to 'crust kilns,' and heated, which causes them to 'sweat' until a browning on the surface ensues, followed by the formation of a thin dry crust all over the cube to a depth of about $\frac{1}{6}$ to $\frac{1}{4}$ of an inch. The lumps are removed from the crusting kilns, the 'crusts' scraped off, and the inner scraped portions, containing from 28–30 p.c. of water, are dried slowly or quickly in large cubes wrapped in paper, or they may be broken into much smaller and more or less regular sized lumps, so as to produce the various 'crystals' and 'lumps,' which are sold as 'domestic laundry starches.' When the starch is to be dried quickly it is broken up quite finely before being placed in the kilns, and when dry it is pulverised by grinding and then bolted. It is also put up as a ground or culinary starch; this is less alkaline than the laundry starches, having received a lighter caustic treatment and better washing with fresh water after it has been treated, the result being a very highly purified commodity.

'Unchemicalled' starch may be dried as

such more or less slowly, and may be ground or not. It is used in the manufacture of baking-powder or as a size in the textile industries. It is also used to a small extent by steam laundries.

All the foregoing starches are thick-boiling; that is, when cooked with boiling water they give rise to very viscous pastes which on cooling form somewhat stiff 'jellies' which break with a glassy fracture.

Up to this point the manufacture of starch is a relatively simple matter, and the material which results very closely resembles in its properties the starch as it originally existed in the raw grain. On account, however, of the heating and action upon it of water, and of the sulphurous acid during steeping, and the alkaline treatments during its further purification, the viscosities of pastes produced from these starches are slightly less than that of starch obtained from the grain which has not been subjected to these influences. Again, the viscosity of unchemicalled starch is greater than that of chemicalled starch, and that of the scrapings from crusted lumps of chemicalled starch somewhat less than that of the inner portions of the lump.

The other starches which may be mentioned are those forming the so-called 'thin boiling' or 'modified' group. These starches, under so-called 'standard' conditions and methods for testing, which are arbitrarily chosen by different workers, give rise, on boiling with water, or solution in a caustic alkali solution, to pastes of very much lower viscosities than thick boiling starches. Hence the name. They may be divided into two subdivisions according to the method of their manufacture.

1. *The drying-in process.*—Unchemicalled starch is suspended in water to about 22°Bé. and a certain quantity of hydrochloric acid is added to the 'milk.' It is then 'boxed' and allowed to drain, the starch—containing 42–43 p.c. of moisture and a small proportion of acid—is broken up and dried; during the drying process, the small proportion of acid partially hydrolyses the starch, causing its viscosity to become less, but in little or no way altering the natural configuration of the starch granules unless temperatures high enough to cause their thorough dextrinisation have been used, or unless they have been heated in the presence of moisture to temperatures above their swelling or gelatinising points—65°–75°C. (149°–167°F.).

2. *The in-suspension process.*—Starch is suspended in water substantially as above, and a certain quantity of sulphuric or hydrochloric acid added. The mass is kept constantly stirred, and is maintained at a temperature well below the gelatinising point of starch, but yet high enough to accelerate the hydrolytic action of the acid on the starch to a reasonable degree, and so to cause a diminution of the viscosity in direct proportion to the length of time, degree of temperature, and strength of acid, to which the starch is subjected. By inspection, even by means of the microscope, modified or thin-boiling starch cannot be discriminated from unmodified or thick-boiling starch.

The maize starch industry of Great Britain (J. Traquair, J. Soc. Chem. Ind. 1912, 1016).—The founding of the maize starch industry in Paisley was due to the fact that in the middle

of last century that town was the centre of several starch-consuming industries.

Potato starch had previously been manufactured in Scotland in several small mills, but these only operated during a few months of the year, and in seasons when potatoes were plentiful and cheap.

Starch was first made in Paisley by Messrs. Wm. Fulton & Co., of Glenfield, for use in their bleaching and finishing works, and in 1847 they sold their process, rights, etc., to Mr. Wm. Wotherspoon, who transferred the factory to Bladda, and then in 1850 to Maxwellton, known from that date as the 'Glenfield Starch Works.'

The raw material employed was East India sago flour, and the process and plant were alike simple. Oak tubs fitted with a removable hand-driven propeller stirrer were used, and in each about 200 lbs. crude sago flour was churned with water. After allowing the sago flour to settle for 6 to 12 hours, the supernatant liquor was decanted, and the starch stirred with sufficient calcium hypochlorite bleach of $4\frac{1}{2}$ °Tw. sp.gr. to give a thin milk, and allowed to stand for at least 12 hours. The bleach was then removed by repeated washings and the process completed by souring with sulphuric acid and washing by decantation two or three times. By removing the top and bottom layers containing respectively the light glutinous impurities, and any sand, &c., a very pure starch was obtained which was dried in the usual way. Glenfield starch was packed in blue paper packets with a green label, and aided by energetic advertising the sales of this starch during the '60's, '70's, and '80's reached a substantial figure, over 500 tubs being in operation.

The introduction of rice starch, however, gradually displaced Glenfield starch from the premier position as a household laundry starch. Sago starches are still made in Glenfield Starch Works for textile and other purposes, but the process and plant have been modernised.

Starch was used to stiffen buckram, and in the early fifties, Messrs. Brown Johnston & Co. (one of the leading buckram makers at that time, and now the only one in Paisley), in searching for a suitable starch other than sago, decided to use Indian corn starch, then being made on a small scale in America. Thus the firm of Messrs. Brown and Polson came into existence and started operations in 1854.

At one time there were some 10 plants manufacturing maize starch in Paisley and neighbourhood; at present there are five. These grind about 600 tons of Indian corn weekly, and produce roughly 20,000 tons of starch and cornflour per annum.

The process of manufacture in Paisley is practically identical with that employed in America, the raw material being maize or Indian corn imported from various and often widely different sources.

23. *Manufacture of starches for edible purposes.*—Alimentary substances may naturally be divided into three well-marked groups—carbohydrates, proteids, and fats; and of these fully two-thirds, or perhaps more, of the food of mankind belongs to the carbohydrate group, of which starch is by far the most important member.

In the raw state, according to Roberts

(Digestive Ferments, p. 17), starch is to man an almost indigestible substance, but when previously subjected to the operation of cooking it is digested with great facility. Diastase has, at best, only a comparatively feeble action on the unbroken starch granule, even at the temperature of the body. By the aid of heat and moisture in the process of cooking the starch granule is much more effectively broken up, and in the gelatinised state is very rapidly attacked and digested by the diastatic juices of the body.

In addition to the large quantities of starch consumed in the natural form—as rice, potatoes, bread, &c.—numerous forms of prepared starches are met with in commerce as articles of food. These differ in a most essential degree from wheat and other cereal flours in that they consist almost entirely of absolutely pure starch granules, which very readily gelatinise and become easily assimilated.

In this country most of the edible starch "cornflour" is made from maize, although some rice is used for the purpose. Tropical and sub-tropical countries furnish arrowroot, sago and tapioca.

24. *Cornflour.*—Although the manufacture of starch from maize has been practised in this country for more than fifty years, the product therefrom—known under various names, such as Indian cornflour, oswego, maizena—has been used chiefly for edible purposes, whilst most of the starch used for other household as well as manufacturing purposes has been that made from wheat and rice.

This industry is centred in Paisley, Scotland, having been first introduced by Polson (Eng. Pat. 1854, 1068). The process of manufacture is now, however, practically identical with that employed in America, the raw material being maize or Indian corn imported from various sources.

25. *Arrowroot starch* or arrowroot is derived from plants of the genus *Maranta*, the most important member of which is *Maranta arundinacea* (Linn.), a native of the West Indies, and which furnishes most of the genuine West Indian arrowroot. Three other species of *Maranta* are also cultivated for the production of starch: *M. nobilis*, *M. Allouia* (Aubl.), which grow in the West Indies, and *M. ramossissima* (Wall.), which is a native of the East Indies.

The arrowroot plant is herbaceous, from 4 to 6 ft. high, and has broad, pointed leaves. The tuberous roots or rhizomes are pointed, covered with scales, and sometimes a foot in length and about the thickness of a finger.

The starch is stored in the rhizomes of the plant, and requires to be extracted and purified to render it fit for market.

The following details of manufacture are taken from a paper by J. W. Macdonald, on 'The Manufacture of Arrowroot Starch in St. Vincent' (J. Soc. Chem. Ind. 6, 334).

The first part of the manufacturing process is to soak the roots in water, to soften the covering and the adhering earth. They are then stripped of the covering and washed, and thrown into a second or rinsing tank. When thoroughly clean they are taken to the pulping machine. The skin is said to contain a resinous matter, which gives a yellow tinge and un-

pleasant flavour to the starch if the latter is not well washed. In former times the roots were skinned with German-silver knives before being pulped. This is said to have produced whiter starch; but as it was so laborious and expensive, it was discontinued. The skinned roots were pulped by subjecting them to great pressure by passing them through an upper, and then a lower and much closer, pair of brass rollers, to break the starch cells. The method of pulping now generally adopted is to feed the clean unskinned roots against a fine saw grater very similar to a potato grater. It is a solid cylinder of hard wood, about 23 ins. diameter and 7 ins. wide. Slits are made by a saw from end to end of the wood at half-inch intervals. Saw blades having 6 to 10 teeth to the inch are then fitted into the slits, and the whole immersed in water to swell the wood and fix the saws. The grater is now fitted into its place very close to a wooden feeding bed. As it revolves several hundred times per minute, it tears the roots into shreds. A great deal, however, depends on the fineness of the teeth and the velocity of the drum.

On account of the very fibrous nature of the pulp, there is considerable difficulty in the sieving or separating the starch from it. The fibres readily gather into lumps and inclose the starch, so that hand-sieving, although very tedious, has to be resorted to. The pulp is first run into a box or sieve, the bottom of which is a sheet of copper or tin punched with holes one-fifth of an inch diameter. While water flows on, the contents are kept thoroughly agitated by hand until all the starch has been washed out. While one strainerful is being washed, another is being filled, so that there should be no delay. However careful one is, there is a loss of starch in the fibre, owing to the presence of small bits of roots which have escaped pulping.

In one factory a stationary half-cylinder is employed. Its under side is pierced with small holes; but there is a slide under this to open or close at will. Inside there are rakes attached to two shafts, which move in opposite directions and cause the rakes to oscillate very rapidly between each other, thereby keeping the fibre always open. The starch water is let out, more water run in, and the operation repeated until all the starch is extracted, after which the fibre is taken out. The great objection to any mechanical washer is the tendency of the fibre to accumulate on the agitators and break them. To get over this difficulty it has been proposed to chop up or slice the roots into small, short pieces, and either rasp them or pass them through metal rollers or millstones, so that the thin disintegrated pulp may flow over mechanical sieves. Although causing a loss of starch, the present method of rasping avoids an undue pulverising of the soft yellow fibre, and so gives a very white starch without much trouble.

From the fibre-strainers the starch water flows consecutively through a series of brass wire sieves of 40, 80, and 100 meshes to the inch; each of these retain small fleshy bits of unpulped root. From the last sieve the water runs into the settling cisterns, which are preferably lined with white glazed tiles to avoid accumulation of slime.

A portion of fibre collected on the finer sieves is used for feeding the animals on the estate; the remainder, and all the coarse fibre, is used as manure. For this purpose it is left in heaps until it decomposes, after which it is distributed on the fields along with pen manure; sometimes ashes and guano are used. The waste water from washing the starch contains a considerable amount of vegetable matter, and gives good results where it is run on the fields; but the extensive application is not practicable. After the starch has settled in the cisterns the water is run off, and more added; the whole is stirred up again, and allowed to settle. This generally suffices to dissolve out soluble matters. At night all the cisterns are drained, and the starch is dug out and taken to a mixing-box, where it is mixed with a small amount of water, then run through another fine sieve into the separating pans. These are small round galvanised cisterns, with smooth perpendicular sides. When filled, the starch-milk is stirred round with a small oar until it is in violent circulation. The oar is withdrawn, and the cisterns left until morning. The stirring has the effect of separating the starch from any remaining impurities. These, being of less specific gravity, settle last, and therefore on the top of the starch. Next morning the water is drained off, and the light, impure starch scraped off the surface. If the earlier parts of the process are carelessly done, this separation may have to be repeated before the starch is quite pure. The impure surface starch contains a large proportion of starch entangled in very fine particles of fibre and broken cell walls. Although this can be dried and exported as an inferior starch, it is generally given to the labourers as a perquisite. It is used in various forms as flour. Poultry and pigs are also fed with it. Weak caustic soda extracts a colouring matter from it, but also precipitates a yellow substance, making it very difficult to separate the starch from it in a pure state.

The pure starch in the separators is now taken out in blocks, and placed on trays for about 12 hours to dry and harden. It is then broken into smaller pieces and taken to the drying house, where it is air-dried, the building being open on all sides for free circulation. It is surrounded, however, with galvanised wire to keep out the small birds which hover about. Inside there is a series of wire shelves over large shallow wooden trays. The top shelf is made of very open wire, the next is closer, and so on, the lowest being the closest. The wet lumps of starch are placed side by side on the top shelf, where they remain until, by the action of the air, they crack up and fall through to the next shelf. In time the whole falls through the lowest shelf, and is in a fine granular state, ready for packing. It contains from 14 to 17 p.c. of water. In cold, wet weather the starch dries very slowly, taking sometimes as long as two weeks. During this time, if it has been imperfectly purified, the lumps get sour and become yellowish. Indeed, the whole process must be as rapid as possible. In the settling cisterns especially, if the starch is left in contact with the impure water too long, its whiteness is affected. The crop lasts from October to May. The name 'arrowroot' is probably derived from

the Indian word *Ara-ruta*, or 'mealy root'; but some say that this root has been confounded with the *Maranta Galanga* (Linn.), which was called the arrowroot on account of its bruised roots being employed as an antidote to the poison of the *Manihot utilissima* (Pohl), used for poisoning arrows.

Regarding the yield of arrowroot, an acre will produce 13,000 to 15,000 lbs. of roots, according to the season; in wet seasons the roots are heavy and moist, and give less starch. A fair average yield is 22 cwt. air-dried starch, with 14 p.c. water, per acre, or about 19 p.c. on good roots. There is no doubt this can be considerably increased by the use of improved pulping and sieving machinery.

The following analyses will give an idea of the constituents of the roots, as well as of the composition of the finished starch:—

	Roots	Starch
Starch	27·07	83·70
Fibre	2·82	0·04
Fat	0·26	0·07
Albumin	1·56	—
Sugar, gum, &c.	4·10	0·18
Ash	1·23	0·14
Water	62·96	15·87
	100·00	100·00

The ash consists of calcium phosphate and alkaline sulphates and chlorides.

Arrowroot starch swells much more readily and with less heat than maize, rice, or wheat starch, and forms a stiffer jelly. It is, therefore, well adapted for sizing and textile purposes. As an article of food it must be regarded as the purest, most digestible, and palatable of the starches.

Methods similar to the above are employed for the extraction of arrowroot starch in the East Indies, Natal, and Queensland.

26. *Cassava: its cultivation and utilisation.*—The cassava plant, known also as manioc and mandioc, is a native of Brazil, where it has been cultivated from time immemorial. It is now grown in almost every part of the tropics, its tuberous roots often forming the chief source of food of the natives. In European countries the best-known product of the plant is tapioca, but in recent years the starch obtained from the roots has been utilised industrially as a source of alcohol, glucose, and dextrin, and as a sizing material for yarns and fabrics. The roots themselves, after suitable preparation, and the residues of the tapioca and starch factories, are largely used as a feeding-stuff for live stock. Within the last few years considerable interest has been taken in the crop as a source of starch in the West Indies, where the roots have long been cultivated as a foodstuff. Factories for the manufacture of cassava starch have already been erected in Jamaica, Trinidad, and elsewhere.

Owing to the large yield per acre and the comparative immunity from disease or pests it seems reasonable to expect that the cassava starch industry will assume considerable proportions.

Varieties.—Cassava is a euphorbiaceous plant belonging to the genus *Manihot*, and is

thus closely related to the Ceara rubber tree (*Manihot Glaziovii*, Muel. Arg.). It is a much-branched shrub which reaches a height of 12 to 16 ft. when allowed to grow naturally, but under cultivation seldom exceeds 6 to 10 ft. The large, swollen root tubers are formed in clusters at the base of the stem; they vary in size and number in the different varieties, but are usually from 1½ to 4 ft. long, and 1½ to 2½ in. in diameter when gathered, though they may attain a much greater size if allowed to grow for several years.

Two forms of cassava are cultivated. That most widely grown throughout the tropics is the 'bitter' cassava, which yields fairly considerable quantities of hydrocyanic acid (prussic acid) from all parts of the root. The second form is the 'sweet' cassava, which also yields hydrocyanic acid, but in this case it is derived mainly from the outer cortical layer or skin. They are frequently regarded as distinct species, the first being *M. utilissima*, Pohl (*Jatropha Manihot*, Linn.; *Janipha Manihot*, Kunth), and the second *M. palmata*, Muel. Arg. (*M. Aipi*, Pohl; *M. dulcis*, Baill; *Jatropha dulcis*, Rottb.). The two plants, however, are extremely difficult to distinguish in the field, and some botanists consider that the sweet cassava is merely a variety of the bitter form evolved in the course of time by cultivation.

Cultivation—climate and situation.—Cassava is essentially a tropical plant, and can only be grown profitably in regions free from frost for at least eight months during the year. Its growth is stopped by a slight frost or even by continued cold weather. Sweet cassava is hardier than the bitter variety, and is consequently almost the only form grown in regions farthest from the equator, such as Paraguay, Southern United States, and Madagascar. In Brazil, according to Peckolt, the bitter varieties are not cultivated below lat. 26° S., the sweet varieties extending as far as 30° S.

The plant thrives best in regions of comparatively slight rainfall, and requires only 14 to 16 ins. of rain per annum. In countries where the rainfall is heavy, it is necessary to select well-drained, light soils to prevent water-logging, which is fatal to the plant. Sufficient moisture is necessary to start the growth of the plant, but once it has become established it will withstand prolonged and extreme drought without injury, and the crop is never a total failure through want of rain.

Although cassava is sometimes cultivated at an altitude of 2500 to 3000 ft., the plant matures earlier and gives heavier yields in the valleys. Better results, too, are obtained in regions near the coast than inland.

Sheltered situations should be chosen for the plantation, as the stems are brittle, and the plant suffers severely in strong winds.

The yield of roots varies considerably, but 8 to 10 tons per acre may be taken as the average. The starch content of the freshly dug roots will run from 18 to 24 p.c., but it is said that special varieties have been cultivated containing as much as 30 p.c. In addition to starch the roots contain from 3 to 6 p.c. of sugars.

Cassava as a catch-crop.—Cassava is frequently grown as a temporary shade plant in young cocoa and coffee plantations. It has

also been recommended for planting on rubber estates, for besides being a source of revenue until the rubber comes into bearing, the deep digging necessary to remove the roots improves the condition of the soil. In Trinidad it has been grown successfully with limes, plants spaced 4 ft. by 4 ft. yielding 5·63 tons of roots per acre in ten or eleven months from the time of planting. Copeland regards cassava as the best catch-crop for planting with coconuts until the latter begin to bear, provided the conditions are suited to it.

It is almost unnecessary to add that when cassava is grown as a catch-crop, it is essential that the fertility of the soil be maintained by proper manuring, so that the main crop is not adversely affected.

Preparation of cassava meal and flour.—In West Africa the roots, as soon as they are dug, are washed and peeled, and then cut into halves longitudinally. The more fibrous central part is removed and the remainder cut up into pieces 3 or 4 in. long. These are spread out in the sun until completely dried, in which condition they keep well for several months. When required for use the dried material is pounded into meal in a wooden mortar, and then sifted to remove any fibre that may be present. Cassava flour is prepared in a somewhat similar way as a domestic product in Florida and other parts of the United States. The roots are peeled, chopped into thin slices or grated, dried in the sun, and then ground into a fine powder. This flour is used as a substitute for wheat flour in making bread and puddings, but is inferior in general nutritive properties. The percentage composition of two such cassava flours, according to Wiley (Bulletin No. 58, 1900, Div. Chem. U.S. Dept. Agric.), was as follows:—

	Cassava flour	
	1.	2.
Moisture	10·56	11·86
Ash	1·86	1·13
Petroleum ether extract (fat)	1·50	0·86
Ether extract (resins and organic acids)	0·64	0·43
Alcohol extract (amides, sugar, and glucosides)	13·69	4·50
Dextrin, gum, &c. (by difference)	2·85	5·63
Crude fibre	2·96	4·15
Proteins	1·31	1·31
Starch	64·63	70·13

As most varieties of cassava plant contain, or yield, hydrocyanic acid, great care must be taken to eliminate this if the resulting meal or starch is to be used for food. Fortunately this is readily achieved in the drying processes.

The content of hydrocyanic acid has been investigated very thoroughly, and the general figure obtained is 0·008 p.c. in the 'sweet' and 0·02 p.c. in the 'bitter.' Both these figures refer to the inner part of the root.

Preparation of starch.—Cassava starch, sometimes known as Brazilian arrowroot, is produced on a considerable scale in Brazil, United States, East Indies, West Africa, and elsewhere. The

chief centres for the production of tapioca are Malaya, Dutch East Indies, and Brazil.

The processes of manufacturing these two products are identical up to a certain point. They consist essentially in grating the cleaned roots sufficiently finely to break the cell walls and so liberate the starch, which is subsequently separated from the fibre and collected in tanks of water. For industrial purposes the starch is then dried, but if tapioca is to be made the wet starch is placed on hot iron plates, which cause the grains to gelatinise and adhere together in lumps.

The machinery required depends on the quantity of roots available. On a small scale all the work can be carried out by hand, but where large quantities are dealt with power-driven machinery must be used. In either case the first essential to success is a plentiful supply of pure, soft water, and the roots must be freshly dug.

There are several types of machines employed for the preparation of cassava starch, and, speaking generally, all the machinery used in a potato starch factory can be employed for cassava, although slight modifications in the character of the grating or pulping machine and of the sieves are necessary, cassava roots being more fibrous than potatoes and the starch grains smaller.

The roots arrive at the factory in all sizes. The larger ones are usually peeled, cut in pieces, and put into a cleaning tank. The smaller roots are placed at once in a washing machine, from which they are transferred automatically to a hopper leading to a pulping machine running at a high speed. This may consist of a cylinder covered with perforated sheet iron, or a drum fitted with finely cut saws. The pulp is carried away in a stream of water to the starch separator, but is sometimes further treated in a mill to complete the disintegration of the cells and ensure the maximum yield of starch. The sieve for separating the starch from the fibre may consist of an oscillating frame covered with fine silk cloth on which water at high pressure is sprayed, or sometimes a horizontally revolving cylinder, covered with fine cloth and kept sprayed with water, is used. As a rule two or three sieves of different mesh are used to facilitate the process. The starch and water from the sieves are run into large settling tanks. The clear water is run off and fresh water added, the starch being stirred with paddles either by hand or mechanically. This process is repeated six or seven times until all foreign matter has been eliminated; the starch is then allowed to settle in tanks of water.

In a process which has been patented recently (Eng. Pat. 530, January 8, 1914) the roots are reduced to fragments and dried rapidly at a temperature below the gelatinising point of the starch until they become brittle. They are next ground to a fine powder which will pass an 80- or 100-mesh sieve. The powder is then moistened and ground into a paste from which the starch is separated in the usual way.

Cassava as a source of glucose.—Considerable quantities of cassava are used in the manufacture of glucose. Either the pulped roots, dried roots, or the starch may be employed for this

purpose. There are several methods of manufacture, which differ in details, but the underlying principle depends on the fact that when starch is boiled with dilute acid it becomes converted into glucose. According to the usual process, cassava pulp is placed in an open vat with water heated by a copper steam coil, and acid is added. The temperature is brought to the boiling-point and the starch and much of the fibre are rendered soluble. The material is then run into a closed copper converter and subjected to steam under pressure for ten minutes or so, until the proper degree of conversion is attained. The liquor is next almost neutralised with sodium carbonate and run through a filter press. The solution of glucose is then filtered through charcoal, concentrated by heating, again run through charcoal, evaporated in a vacuum pan, and the glucose finally cooled and barrelled. By this process glucose can be obtained to the extent of about 30 p.c. of the weight of the fresh root.

Other industrial applications of cassava starch.—Cassava starch is stated to be inferior to other kinds of starch for sizing cotton yarn, as it yields a paste of somewhat feeble adhesive properties. For medium and heavy sizing it may be mixed with some other material with stronger adhesive power, such as wheat flour or maize starch. Tracy (Farmers' Bulletin, No. 167, 1903, U.S. Dept. Agric.) states that the whole of the output of the cassava starch factories existing in Florida at the time he wrote was sold to cotton factories, where it was used in making sizing for various classes of goods.

Trade in cassava products.—Little reliable information is available as to the trade in the various cassava products, as the official returns do not clearly differentiate between them, but the following statistics will serve to indicate the magnitude of the industry.

Imports into consuming countries.—In 1914 the United Kingdom imported 299,097 cwts. of 'cassava powder and tapioca,' valued at £235,817. Of this quantity 192,254 cwts. came from the Straits Settlements and dependencies, including Labuan, and 95,396 cwts. from Java. In the same year this country also imported 566,528 cwts. of 'tapioca flour' (cassava starch), of value £251,883; 424,669 cwts. coming from Java, 96,538 cwts. from the Netherlands, and 40,411 cwts. from the Straits Settlements.

The imports of cassava products into France in 1913 were as follows:—

	Quantity cwts.	Value £	Chief countries of origin
Cassava flour ¹	94,660	66,382	East Indies
Dried Cassava	395,252	139,552	French colonies
Crude Tapioca	139,125	127,358	East Indies
Crushed Tapioca	13,391	13,610	„ „

Cassava products are not shown separately in the Hamburg trade returns, but the imports of tapioca and sago into that port in 1913 amounted to 78,673 cwts., valued at £61,328, the greater part of which came from the East Indies.

¹ Including sago and salep (prepared from the roots of an orchid).

The total imports of cassava products into the United States in 1914 amounted to 636,650 cwts., valued at £331,378. These come mainly from the Dutch East Indies.

The exports of tapioca from the Federated Malay States have decreased considerably in recent years. In 1909 and 1910, 269,837 and 172,637 cwts. respectively were exported, whilst in 1913 and 1914 the quantity was only 58,634 and 58,368 cwts.; the values in the two last-named years were £23,232 and £24,023. The kind of tapioca exported and the countries of destination are not recorded in the official trade returns.

Both pearl and flake tapioca, as well as cassava starch, are produced in the Federated Malay States, and most of the exports are shipped *via* the Straits Settlements.

Dutch possessions.—The exports of cassava products from Java and Madura in 1913 were as follows:—

	Cwts.
Tapioca flake . . .	206,000
„ pearl . . .	15,400
Cassava starch . . .	1,048,000
Dried roots . . .	508,000
Refuse from factories . . .	278,000

Of the above quantity of cassava starch the United States took 440,000 cwts., the United Kingdom being the next largest consumer, taking about 300,000 cwts. annually. Of the other products the United Kingdom takes 58 p.c. of the total exported.

Cassava products are also exported from the east coast of Sumatra, the quantity of cassava starch exported in 1912 amounting to 18,660 cwts.

French possessions.—The chief French colony producing cassava is Madagascar, which in 1912 exported 22,378 metric tons of dried cassava, valued at £116,928, and 682 metric tons of cassava meal, valued at £6418. In the same year, 1544 metric tons of tapioca, of value £33,127, and 329 metric tons of cassava starch, of value £2476, were exported from Reunion, and 771 metric tons of starch, valued at £7706, from Indo-China. Most of the produce of the French possessions is exported to France.

Brazil.—Recent statistics relating to the exports of cassava products from Brazil are not available. The quantities exported in 1908 and 1909 were as follows:—

	1908 Metric tons	1909 Metric tons
Cassava starch . . .	5458	5161
Tapioca . . .	248	141

A certain amount of dried cassava is also exported from Brazil.

A very complete report upon cassava will be found in Bull. Imp. Inst. vol. 13, No. 4, from which much of this information has been obtained.

27. *Curcuma starch.*—In the East Indies a starch is prepared from the tuberous root of *Curcuma angustifolia* (Roxb.), which is sometimes known as East India arrowroot, and said to be rather extensively manufactured in Travancore and other parts of North-West India.

27. *Arum starch*.—A starch very much resembling cassava starch, and which was used as a substitute for arrowroot, and known in the market as Portland arrowroot, was obtained from the roots of the wild arum, or *Arum maculatum* (Linn.), this plant being formerly cultivated in the Island of Portland for this purpose.

29. *Tous-les-mois*.—This starch, the granules of which are the largest known, is extracted from the rhizomes of the *Canna edulis* (Ker-Gawl), a native of the West Indies, principally at St. Kitts. That which is imported into this country is used partly in the manufacture of cocoa and partly in the preparation of food for infants.

30. *Sago*.—This is the name given in commerce to a prepared starch obtained from the pith of several varieties of palms, which are indigenous to the Malayan Archipelago, the Philippine Islands, and parts of India, wherever there is a soil suitable for their cultivation. This consists of marsh or bog land, composed of decayed vegetables, near the sea. The principal species are the following: *Metroxylon Sagus* (Roxb.), *Raphia pedunculata* (Beauv.), *Borassus flabellifer* (Linn.), and *Arenga saccharifera* (Labill.).

All these palms propagate themselves by lateral shoots as well as by seed, so that a sago plantation, when once formed, may be said to be perpetual. The growth is slow at first, but when once fairly started proceeds rapidly, until a height of some 20 to 30 feet is attained by the stem.

The sago tree, when cut down and the top severed from it, represents a cylinder about 20 ins. in diameter, and from 15 to 20 ft. in length, consisting essentially of a hard woody tube, the interior of which is filled with starch granules intermixed with fibrous matter. From such a tree about 700 lbs. of starch would be extracted, so that three such trees would yield nearly double as much food material as one acre of wheat. Sago is, however, far from being either so palatable or nutritious as it is prolific, and even where it is more abundant is never preferred to rice.

By far the greater portion of sago imported into this country comes in the raw state as sago flour, and is used to a very large extent in the manufacture of glucose. Singapore is the headquarters for exportation of sago, both raw and manufactured being brought there from the islands to the eastward, principally from the north-west coast of Borneo and the north-east of Sumatra, with its adjacent isles from Siak to Indragari, as well as from many other places more distant.

To obtain the starch or flour, the trees, as soon as they have arrived at a suitable stage of growth, are cut down close to the roots, the stems sawn into pieces 7 or 8 ft. long, which are split open and the pith extracted. This is then pounded up in wooden mortars so as to reduce it to powder, agitated with water in a trough, run through sieves to free the starch from cellular tissue and fibrous matter, allowed to settle, and, after washing several times with water, is dried and sold as sago flour.

What is known as granulated or pearl sago is prepared from sago flour in the following

manner: The flour is made into a stiff paste with water, and rubbed through a metal sieve into a heated, very shallow, copper or iron pan, greased inside with vegetable fat. During the process of heating, the starch granules are kept constantly agitated, a portion of them swelling and becoming pasty serve to bind the remainder of the granules together. The resulting cohering particles obtained in this way are called pearl sago, of which two kinds are known in commerce, one consisting of small grains about the size of rape seed, and the other of grains about two or three times the size.

Granulated sago appears to have been introduced into Europe in the early part of the eighteenth century, but there is reason to believe that the starch from the sago palm has been used as an article of food by the natives of those countries in which it grows from a very remote period.

A sample of pearl sago gave on analysis:

Starch	84·64
Water	15·22
Mineral matter	0·14
Total	100·00

In later times, in Germany and France, sago has been made from potato starch, and introduced into commerce as 'Indian sago,' the best specimens of these imitations surpassing real sago in appearance and whiteness; so that the question arises, Is there any essential difference between a European imitation and the real sago of the tropics? Opinions as to goodness of flavour differ, and in reference to the nutritive values of the two, there have been no scientific investigations. *A priori*, it is not impossible that the nutrient value of the real is greater than that of the artificial, since the former contains more granulose. However, the difference between the relative values of the two is not nearly so great as the difference in price, which stands almost as 1:2.

Sago has the property of swelling up in hot fluids without losing its coherence; the granules do not fall to pieces, but appear as transparent and gelatinous, but not sticky, spheroids.

31. *Inulin*.—In the tubers of the dahlia, Jerusalem artichoke, and other plants of a similar character, there occurs an amylaceous substance which bears a very close resemblance to starch, having identically the same ultimate composition, and which, indeed, for all practical purposes may be regarded as another form of starch.

To this substance the name of *inulin* has been given. It is a white hygroscopic powder or sphæro-crystals, insoluble in absolute alcohol and sparingly soluble in dilute alcohol. It has the power of reducing ammoniacal silver nitrate.

Kiliani (Annalen, 205, 145) prepares inulin as follows. Roots of *Dahlia variabilis* (Desf.) are well washed, and, after being rasped, are boiled with water in the presence of sodium carbonate. The liquid obtained is cooled by means of a freezing mixture, allowed to stand some time, and the precipitate which settles out dissolved in hot water, filtered while hot, and again exposed to a freezing mixture. This

process is repeated three or four times, after which the inulin is obtained as a perfectly white substance. It is then treated with alcohol, whereby any l  vulose that may be present is removed, and the inulin finally dried over sulphuric acid *in vacuo*.

Inulin is not acted upon by diastase, but is converted into l  vulose when heated with dilute acids.

During the European war appreciable quantities of inulin were extracted from artichokes and other plants in the laboratories of St. Andrews University, and its extraction and conversion to fructose were also undertaken elsewhere on a larger scale.

Under customary treatment inulin gives a poor yield of solid fructose, the bulk of the product consisting of an uncrystallisable syrup, condensation products from γ -fructose.

32. *Lichen starch*.—In Iceland moss there occurs a form of starch easily soluble in water, from which it is thrown down as a flocculent precipitate by alcohol, and which gives the characteristic blue coloration with iodine. It rotates polarised light strongly to the right, and is readily converted by diastase into dextrin and maltose. Lichen starch, therefore, appears to be a soluble, unorganised modification of ordinary starch (J. Soc. Chem. Ind. 1917, 556). Reference may be made to a paper by O. Hesse (J. Prakt. Chem. 1916, 94, 227).

33. *Glycogen*.—In the livers of most animals there is produced a white amorphous substance which forms an opalescent solution with water, from which it is precipitated by alcohol, and is transformed into dextrin and maltose by the action of diastase, and to which the name of glycogen has been given. It has a formula $C_6H_{10}O_5$, specific rotatory power $[\alpha]_D + 197^\circ$, and gives a wine-red coloration with iodine. It may be regarded in every sense as an exact counterpart of soluble starch, and is considered to be reserve starch material elaborated from the sugars and other carbohydrates consumed as food.

34. *Detection of starch*.—The presence of starch existing in the solid state in any substance is most readily detected by microscopic examination, supplemented, where necessary, by the addition of iodine solution to the slide, when the characteristic blue coloration is at once observed if any starch granules are present. In this way the presence of starch in chlorophyll granules may be readily detected by Sachs' method (Chem. Zentr. 1884, 945). The fresh green leaves are plunged into boiling water for 10 minutes; certain soluble substances are thereby extracted, whilst the starch and colouring matter of the chlorophyll grains remain intact. A short immersion in 96 p.c. alcohol now removes the green colouring matter and certain bodies soluble in alcohol, leaving the starch behind in the colourless tissue, the decoloration proceeding more rapidly in sunlight or warm alcohol than in the dark and cold. After this treatment the leaves are placed in a strong solution of iodine, made by dissolving iodine in alcohol, and then diluting with distilled water until the liquid has a dark-brown colour. They are allowed to remain in this liquid for about an hour, or until they no longer acquire

colour. If no starch is present the leaves are simply stained yellow; if they are stained slightly black, very little starch is present. If a large quantity of starch exists in the cells, the tissue appears blue-black or black, with a metallic lustre, the venation appearing as a pale network in the dark ground. By this means the absence of starch from etiolated leaves, from the white portions of variegated foliage, and from those portions of the leaf which have been covered by paper or tin-foil, may be readily demonstrated.

When a sample of a substance supposed to contain starch is to be examined under the microscope, it is first reduced to a fine powder, if not already in that state; a small quantity of it is then mixed with some water in a watch-glass by means of a glass rod, and a drop of the mixture placed on the slide, a cover-glass put on, any superfluous moisture round the edges of the cover-glass carefully removed with blotting-paper, and the slide next placed under the microscope; the stage should be illuminated with rather oblique light, a $\frac{1}{4}$ or $\frac{1}{5}$ inch objective, with a B eye-piece, being the most suitable magnifying power to employ.

The following points should be observed: the size and form of the granules, the position and character of the hilum, the nature of the stri   or concentric rings, and the appearance presented by the granules under polarised light. In the latter case, it is advisable to mount the sample in glycerin instead of in water; a red-green selenite plate may also be advantageously employed. It is only by careful microscopical examination that one particular form of starch can be differentiated from another, and it is comparatively easy when only one kind of starch is present; but when mixtures of different starches occur in the same sample, the detection of each particular one becomes a matter of some difficulty.

The following method, as given by Bell (Chemistry of Foods, 2, 151), appears to be practicable for most of the commonly occurring varieties:—

To ensure the homogeneousness of the sample, it is first rubbed in a mortar, and passed several times through a sieve. A small quantity, say 0.5 of a grain, is then weighed out and placed upon a glass slide, where it is worked into a thin paste with about two drops of water. A thin covering-glass, measuring about $1\frac{1}{2}$ inch by 1 inch, is then placed over the paste, and moved about the slide until the paste is equally distributed and all under the covering-glass. With a $\frac{1}{4}$ -inch objective and B-eyepiece the number of granules of foreign starch is counted in nine 'fields,' as fairly as possible representing the entire slide. The process is repeated until a correct idea of the composition of the sample is obtained.

Standard mixtures approximately representing the sample are then made up and treated in exactly the same way, and, from a comparison of the results, the percentage of foreign starch is computed.

When the percentage of foreign starch is large it is advantageous, in order to facilitate the counting of the granules, to insert in the eye-piece a slide accurately divided into squares.

In cases where the granules of added starch are so small and numerous that it is impossible to count them, as with rice starch, a similar process of preparing the slides is followed, and as correct an estimate of the foreign starch is made as is possible by a comparison of the appearance of the sample with that of the standard mixtures.

It is often advisable to use a dilute solution of iodine instead of water in preparing the slides for examination, as the resulting coloration of the starch granules renders them more distinctly visible.

Sometimes it is desirable to remove the colouring matter from the solid substance, and if cold water fails to effect this, alcohol and other solvents should be tried. Successive treatments of the substance with cold water and alcohol, however, will usually render the starch observable microscopically without having recourse to other solvents.

As an aid to their microscopical examination and recognition, Allen (Commercial Organic Analysis, 335; revised edition 1909, 411), following Muter, arranges the starches into five classes, having the following general characteristics:—

I. THE POTATO GROUP includes such oval or ovate starches as give a play of colour when examined by polarised light and selenite plate, and having the hilum and concentric rings clearly visible.

II. THE LEGUMINOUS STARCHES comprise such round or oval starches as give little or no colour with polarised light, have concentric rings all but invisible, although becoming apparent, in many cases, on treating the starch with chromic acid, while the hilum is well marked, and cracked or stellate.¹

III. THE WHEAT GROUP comprises those round or oval starches having both hilum and concentric rings invisible in the majority of granules. It includes starches from wheat and some other cereals, and a variety of starches from medicinal plants, such as jalap, rhubarb, senega, &c.²

IV. THE SAGO GROUP comprises those starches of which all the granules are truncated at one end. It includes some starches used for food, together with those from belladonna, colchicum, scammony, podophyllum, canella, aconite, cassia, and cinnamon.

V. THE RICE GROUP contains the starches all the granules of which are polygonal in form. It includes the starches from oats, buckwheat, rice, pepper, and ipecacuanha.

35. *Microscopical appearance of different varieties of starch.*—The microscopical appearance of the different varieties of starch granules is shown in the following illustrations, which are taken from Dr. Bell's Chemistry of Foods, Pt. II.

CLASS I.—(a) *Canna*, or *Tous les mois* (Fig. 18).—The granules of this starch are the largest known, are ovate in form, rounded at one end, and more or less pointed at the other, near which

is situated the circular hilum. The rings are well marked, but not complete.

(b) *Potato* (Fig. 19).—Granules vary much in form, the smaller ones being more or less spherical, whilst the larger are ovate or oyster-shaped. The hilum, which may be circular or stellate, is generally near the smaller end. In the larger granules the concentric rings are very distinct and complete.

(c) *Maranta*, or *Arrowroot*.—According to Bell, *Bermuda arrowroot* (Fig. 20) may be taken as the most perfect type of a maranta starch. In no other kind of arrowroot do the granules so generally exhibit an irregularly oval form, with the peculiar, small, nipple-like projection near one end, where also is situated the hilum, which is either circular or linear. The rings are concentric and numerous, always visible, but not strongly marked.

(d) *Natal arrowroot* (Fig. 21), as compared with Bermuda, may be taken as an example of the divergence which occurs in the form, size, and general appearance of the starch granules yielded by different varieties of maranta. The hilum is generally linear. The rings are very distinct under water.

CLASS II.—*Bean*, *Pea*, and *Lentil* (Figs. 22, 23).—These starches are very similar in appearance, and not distinguishable from one another in mixtures. The granules are oblong, kidney-shaped, and irregularly formed, most of them having a longitudinal cavity running along each granule lengthwise, and from which, in many instances, furrows diverge to the right and left, imparting to their surfaces a fractured appearance.

CLASS III.—*Wheat* (Fig. 24).—The granules, which are nearly circular, present a flattened appearance under the microscope, and are generally of two sizes—large and small. Hilum central; rings concentric and very faintly marked.

Barley (Fig. 25).—The granules are very similar to those of wheat, but rather more irregular in shape.

Rye (Fig. 26).—The granules of this starch are larger than those of wheat or barley, are more circular in form, and present a flattened appearance and fractured surface. The hilum in the majority of the granules is stellate.

CLASS IV.—*Sago* (Fig. 27).—The granules are elongated, rounded at one end and truncated at the other. Hilum circular, stellate, or linear, near convex end. The rings are concentric, numerous, and but faintly visible.

Cassava (Fig. 28).—The granules are similar to those of sago, but not so elongated, presenting more the appearance of a kettledrum. The hilum, which is well defined, is situated near the centre.

Arum (Fig. 29).—Somewhat like cassava, but much smaller.

CLASS V.—*Rice* (Fig. 30). The granules of this starch are the smallest of all the commercial starches, and are pentagonal or hexagonal in form. Hilum extremely minute, but distinct with a very high power.

Maize (Fig. 31).—The granules are polygonal, but approaching to circular, and are intermediate in size and general appearance between the starch granules of wheat and oats. The hilum is central and stellate.

¹ All these starches present very close resemblances, and are generally indistinguishable from each other when in admixture.

² The cereal starches may be divided into two well-defined groups, wheat, barley, and rye starches being circular, or nearly so, while the starches of rice, maize, buckwheat, and oat are polygonal.

Oat (Fig. 32).—The granules are triangular to hexagonal in form. Both rings and hilum are invisible except under very high powers.

For illustrations of various other forms of starch granules, see under 'Starch' in Payen's *Chimie Industrielle*.

36. *Estimation of starch*.—The accurate estimation of starch is a matter of considerable difficulty, owing to a combination of circumstances. The first of these is that there is no method known of making a direct estimation, which will give trustworthy results, and therefore it is always necessary to convert starch into bodies which can be so determined; next, starches of different origin differ in resistance to agents used for this conversion; and thirdly, starch is commonly associated in plant material with a variety of bodies also liable to be affected by the conversion, and so to vitiate the results.

Because of these difficulties, starch content is often arrived at by difference, after estimation of the other substances present, a method open to obvious objections. Where a direct estimation is attempted, it follows from what has been said, that the analytical methods used will depend on the degree of accuracy required, and on the nature of the starch-containing material. As stated above, the first step is to convert the starch into soluble bodies—dextrins and sugars—which can then be separated from the other substances associated with it, and finally estimated.

Two methods are commonly used to affect the conversion, either acid hydrolysis or treatment with diastase. The former can be used where great accuracy is not required, although it can be made to give fairly reliable results on certain classes of material. It will now be described.

By boiling with 2 or 3 p.c. hydrochloric acid for a few hours, starch is converted into dextrose, which is estimated by means of (Barreswil's) Fehling's solution (see *Sugar Analysis*, Art. Sugar). Even with pure starch, the method gives results about 5 p.c. too low, owing to some decomposition of the dextrose, and it is still more unreliable if the starch is associated, as in plant material, with other bodies which may also use sugars capable of reducing Fehling's solution. The standard method of carrying out the estimation, known as Sachsse's (official in the U.S.A.), is as follows (Bureau of Chemistry, Bulletin 107, revised 1912): 3 grms. of the material are extracted with 50 c.c. of cold water for an hour with frequent stirring. The residue is collected on a filter and washed with water sufficient to bring the filtrate up to 250 c.c. If the solution is difficult to filter, 2 c.c. of alumina cream are added. The soluble carbohydrates are determined in the filtrate both before and after inversion.

The insoluble residue is heated for $2\frac{1}{2}$ hours with 200 c.c. of water and 20 c.c. hydrochloric acid (sp.gr. 1.125) in a flask with a reflux condenser, the mixture cooled, nearly neutralised with sodium carbonate or sodium hydroxide, made up to 250 c.c., filtered, and the dextrose determined in an aliquot portion of the filtrate, a correction being made for the soluble carbohydrate originally present. The weight of

dextrose, multiplied by 0.9, gives the weight of starch.

Instead of estimating the reducing power of the solution, its optical rotation can be determined and used as the basis of calculation if a suitable modification of the preliminary acid treatment be made, and this method has been largely used for estimating starch in cereals.

Lintner's method of carrying it out is as follows: 5 grms. of the cereal previously reduced to the finest possible state of division are triturated in a mortar with 20 c.c. of water until no lumps remain; 40 c.c. of hydrochloric acid of sp.gr. 1.15 are then added, with continued trituration, in portions of about 5 c.c. at a time, and the mixture allowed to stand for about 10 mins. The liquid is then washed into a 200 c.c. calibrated flask by means of hydrochloric acid of sp.gr. 1.1; 10 c.c. of a 4 p.c. solution of phosphotungstic acid are added to precipitate the proteins, and the volume made up to 200 c.c. with the diluted acid. After mixing, the contents of the flask are transferred to a wide-necked, stoppered bottle, thoroughly shaken and filtered. The clear filtrate is examined by the polarimeter in a 200 mm. tube.

The concentration of the soluble starch is calculated on the basis of $[\alpha]_D = 200.3^\circ$ for barley starch dissolved in hydrochloric acid at 20° . Provided the liquid be not allowed to remain longer than 2 hours before polarising, no decrease in the rotatory power need be feared. The method gives results 4 to 6 p.c. lower than the acid conversion process owing to the pentosans, &c., being counted in the latter process.

Wenglein (Z. ges. Brauw. 1908, 31, 53) proposes the substitution of sulphuric acid of sp.gr. 1.70 for hydrochloric acid in Lintner's process, and washes with acid of sp.gr. 1.30. The method of procedure is otherwise the same, but the solutions can be kept 8 hours unchanged before polarisation. For starch in sulphuric acid, the $[\alpha]_D = 191.7^\circ$.

The above methods neglect the optical activity due to constituents other than starch in the material under examination. Where these other constituents are present in appreciable quantities, correct results will not be obtained, and Ewer proposes a method in which allowance is made for this error, which is as follows:

25 c.c. of glacial acetic acid are run into a 200 c.c. flask without wetting the neck. Five grms. of the finely ground material are then added and the flask closed and vigorously shaken until the mixture is uniform. The stopper and neck of the flask are then washed down with a further 20 c.c. of glacial acetic acid and the flask placed in a boiling water bath for 10 minutes; 10 c.c. of dilute hydrochloric acid (1 in 10) are added, and the flask is left in the water bath for exactly 6 mins., being shaken round every minute. Hot water is then added to make the volume up to 180 c.c. and the mixture is heated for a further 18 mins. in the boiling water bath. The solution is finally cooled, clarified by the addition of 2.5 c.c. of potassium ferrocyanide, made up to the mark with water, filtered and polarised. If the filtrate cannot be obtained clear, a few



FIG. 18.



FIG. 19.



FIG. 20.

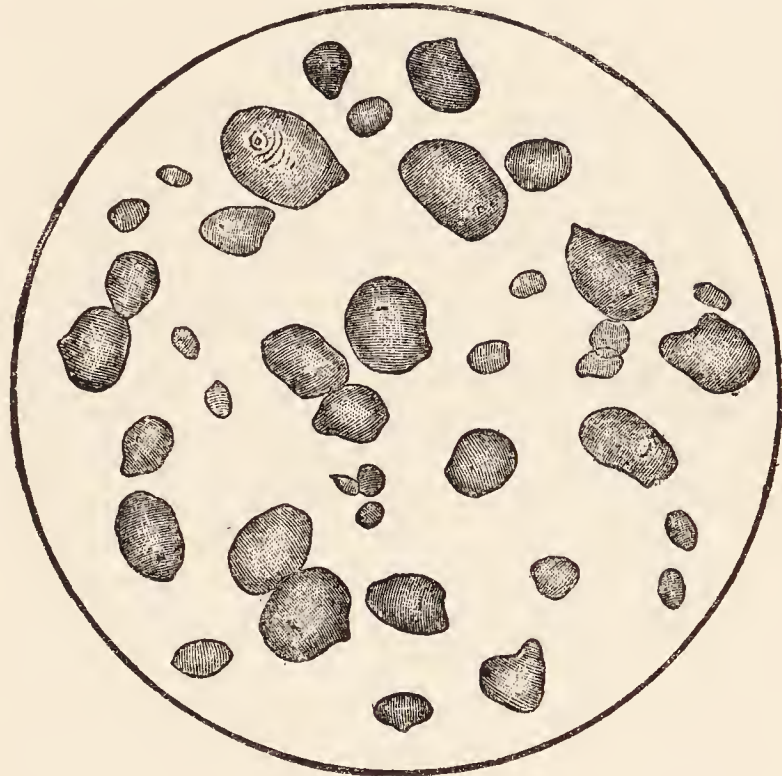


FIG. 21.



FIG. 22.

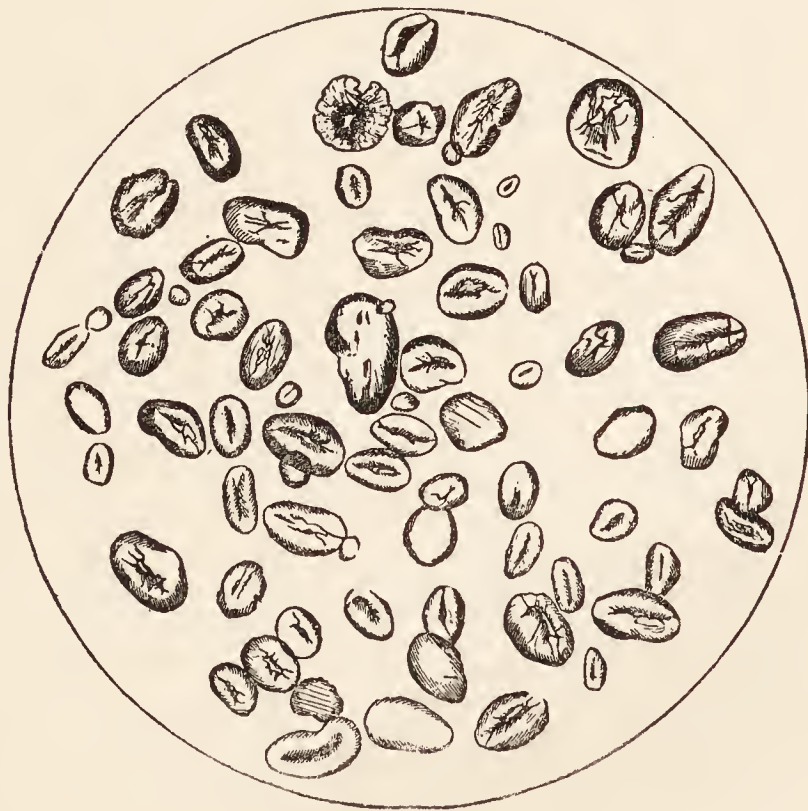


FIG. 23.

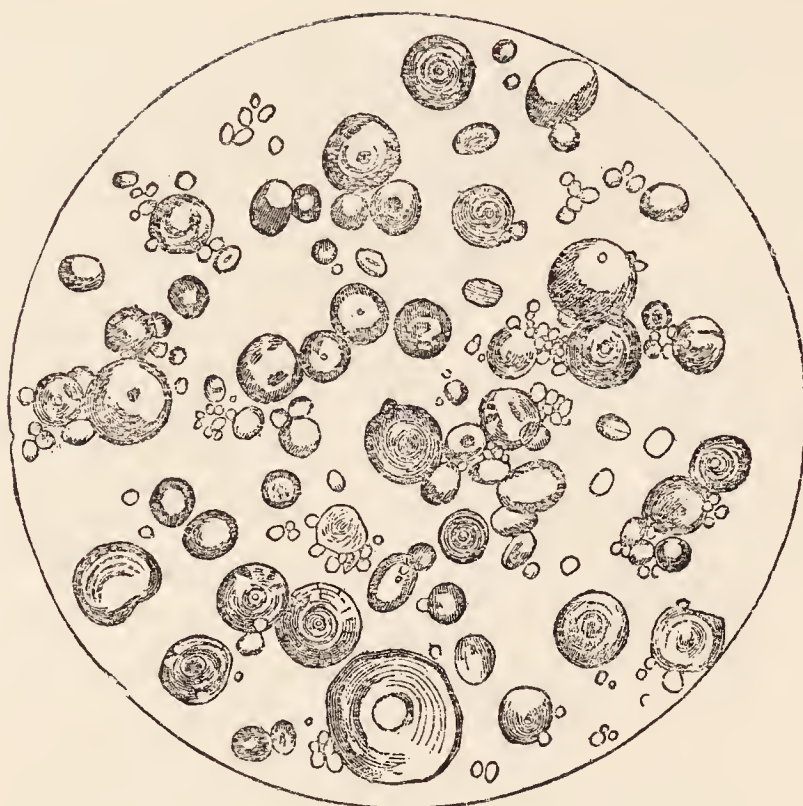


FIG. 24.



FIG. 25.

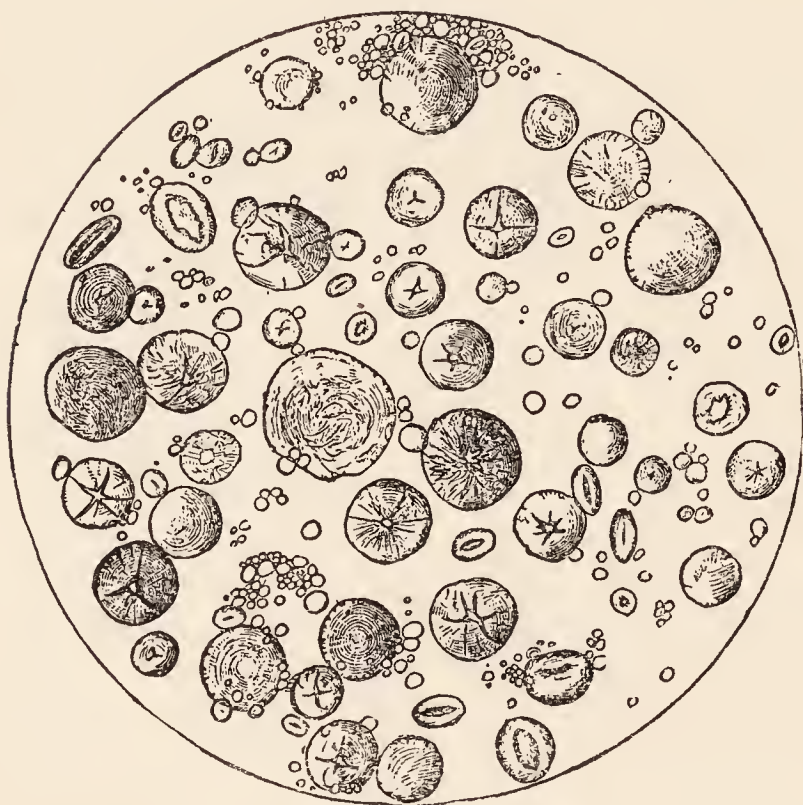


FIG. 26.



FIG. 27.

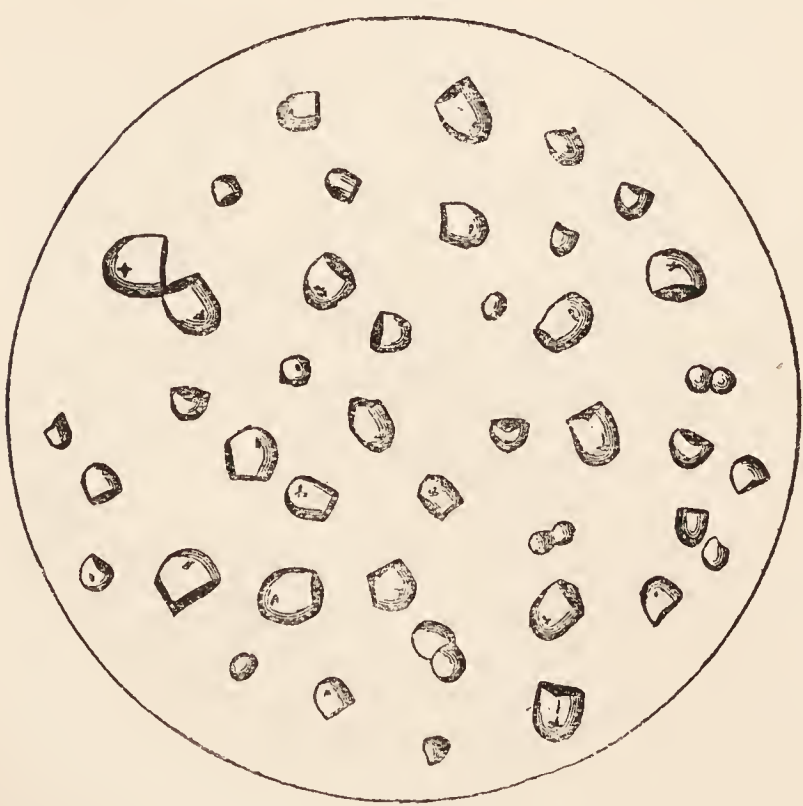


FIG. 28.

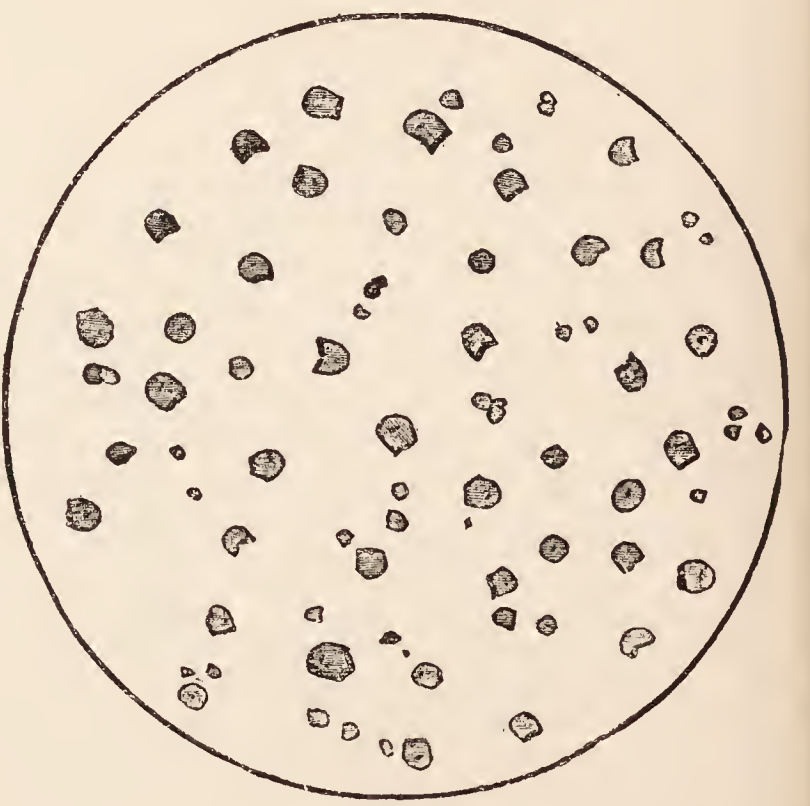


FIG. 29.

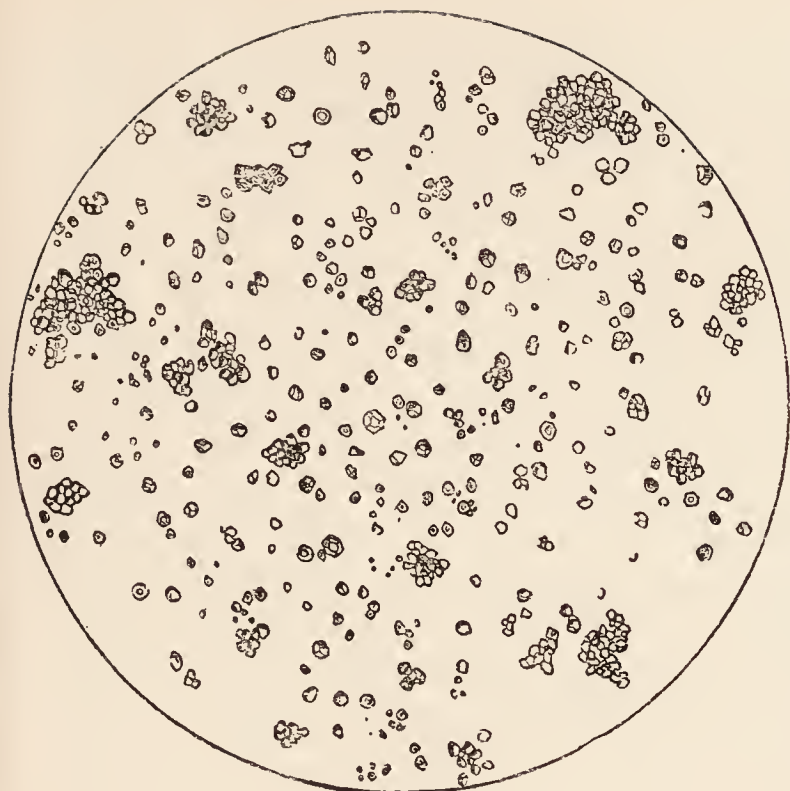


FIG. 30.

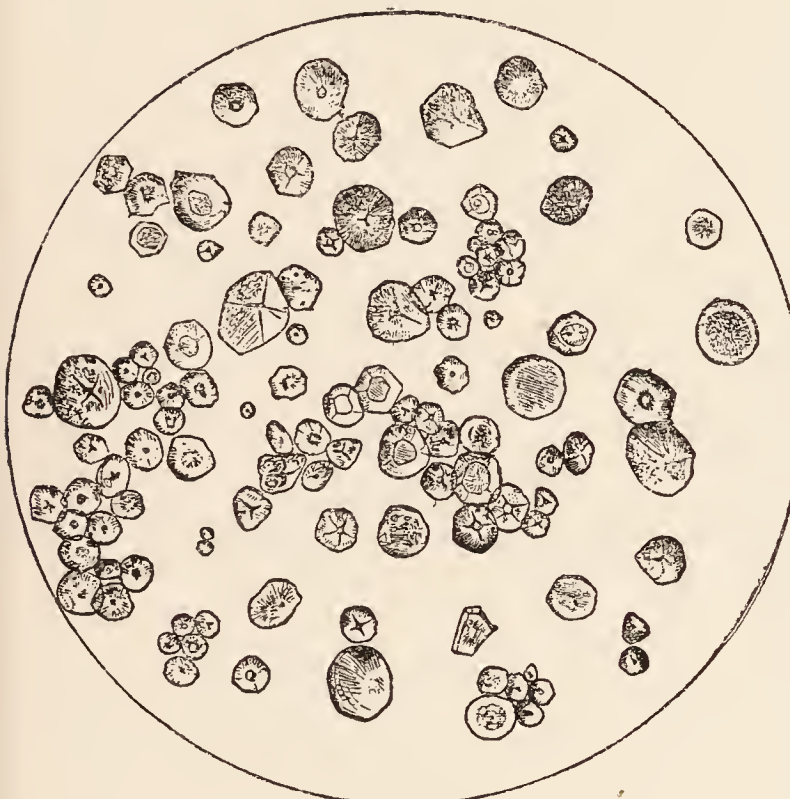


FIG. 31.

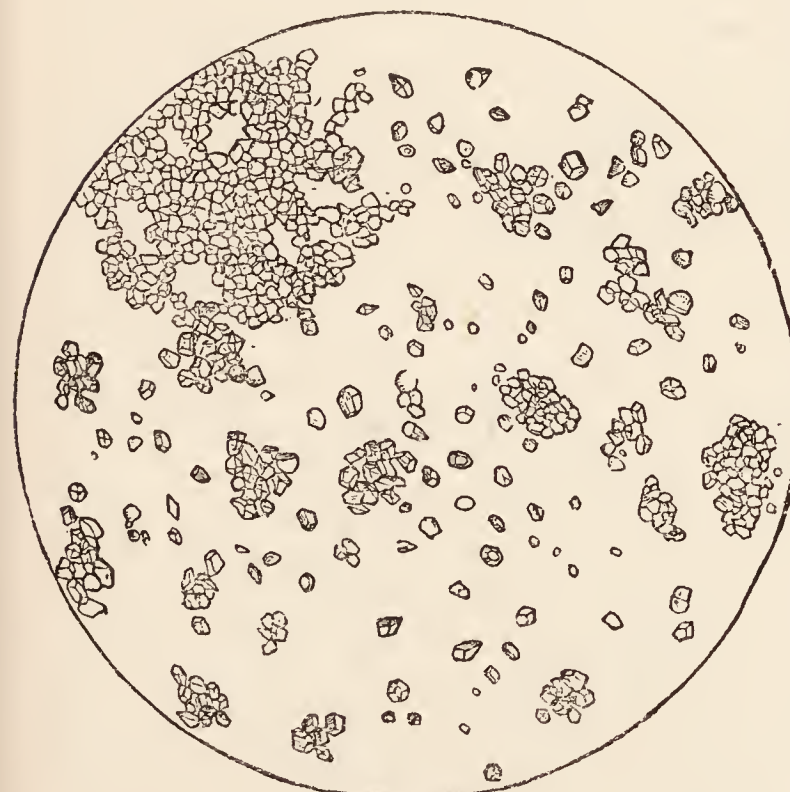


FIG. 32.

crystals of zinc sulphate can be added to assist clarification.

A blank experiment is then made to correct for the optically active bodies other than starch; this is conducted as follows: 5 grms. of the finely ground material are transferred to a 100 c.c. flask with 70 c.c. of water at about 50° , and the whole thoroughly mixed by vigorous shaking. This is digested at the ordinary temperature for one hour, then 25 c.c. of glacial acetic acid are added and the digestion continued at the same temperature for half an hour, during which the temperature is adjusted to 15.5° , the ferrocyanide added as before, and the liquid made up to the 100 c.c. mark, mixed, filtered and polarised.

Ewer's method has more recently been modified as follows (J. Soc. Chem. Ind. 37, 69a): The grain, or other substance, is ground to pass a 1 mm. sieve and 2.5 grms. of the powder is placed in a 100 c.c. flask together with 25 c.c. of 1.124 p.c. hydrochloric acid. After the mixture has been shaken, the sides of the flask are rinsed down with a further 25 c.c. of the hydrochloric acid, and the flask is placed in a boiling water bath for exactly 15 mins.; during the first 3 mins. the flask is shaken. Cold water is then added so as to make the volume up to about 90 c.c., the mixture is cooled to room temperature, from 0.25 to 1.5 c.c. of sodium or ammonium molybdate solution (containing 120 grms. of MoO_3 per litre) is added, the whole is diluted to 100 c.c., filtered, and the filtrate polarised in a 200 mm. tube. The reading in angular degrees is multiplied by 10.94, or in Ventzke degrees by 3.79, to obtain the percentage quantity of starch. A correction for water-soluble optically active substances is made by digesting 12.5 grms. of the sample with 250 c.c. of cold water for one hour, filtering the mixture, treating 50 c.c. of the filtrate with 2.1 c.c. of hydrochloric acid (sp.gr. 1.215), and heating this mixture in a boiling water bath for 15 mins. The mixture is then cooled, clarified, and polarised as before, the reading obtained being deducted from that observed in the main determination.

The second method of estimating starch is to convert it into a mixture of dextrin and maltose by means of diastase, and then by determining both the rotation and the cupric reducing power of the filtered solution, to calculate the amounts of these two bodies present, and hence the amount of starch from which these were derived. This method is due to O'Sullivan, and the estimation of starch in cereals by it is carried out thus:—

A fair sample of the grain is taken, and of this 5.1 grms. are weighed roughly, and ground fine in a coffee-mill, kept clean for the purpose. Of the finely-ground flour, 5 grms. or thereabouts, accurately weighed, are introduced into a wide-necked flask, capable of holding 100 to 120 c.c. The flour is just saturated with alcohol, sp.gr. 0.82, and then 20 to 25 c.c. ether added. The flask is corked and put aside for a few hours, the deposit being shaken occasionally. The clear ethereal solution is decanted through a filter, and the residue washed by decantation with three or four fresh quantities of ether, the washings being passed through the filter. To the residue 80 to 90 c.c. alcohol, sp.gr. 0.90, are

added, and the mixture kept at 35° – 38° for a few hours, with occasional shaking. The alcoholic solution, when clear, is decanted through the filter used in filtering the ether solution, and the residue washed a few times by decantation with alcohol, of the strength and at the temperature indicated. The residue in the flask, and any little that may have been decanted on the filter, is then washed with water into a beaker capable of holding half a litre, and the beaker is nearly filled with water. In about 24 hours the supernatant liquid becomes clear, when it can be gradually decanted through a filter. The solution filters bright, but in the case of barley and oats exceedingly slowly at times; the malted grains, as well as wheat, rye, maize, and rice, yield solutions requiring no excessive time to filter. The residue is repeatedly washed with water at 35° – 38° , but even this treatment does not completely free barley and oats from α -amylan, which dissolves with the greatest difficulty at this temperature. The residue is then transferred to a 100 c.c. beaker, and the portion adhering to the filter washed by opening the filter paper on a glass tube, and removing every particle by means of a camel's-hair brush, cut short, and a fine-spouted washbottle. When the transference is completed, the beaker, which should not now contain more than 40 to 45 c.c. of liquid, is heated for a few minutes in the water-bath, care being taken to stir well when the starch is gelatinising, to prevent 'balling' or unequal gelatinisation. After this the beaker, still in the bath, is cooled to 62° – 63° , and 0.025 to 0.35 gm. diastase, dissolved in a few c.c. of water, added. A trace of the solution ceases in a short time to give a blue colour with iodine, the starch being completely decomposed and dissolved. Yet it is well to continue the digestion at 62° – 63° for an hour, as the solution, as a rule, filters better. At the end of that time the contents of the beaker are boiled for 8 or 10 minutes, thrown on to a filter, and the filtrate received in a 100 c.c. measuring flask. The residue is carefully washed with successive small quantities of boiling water. When the flask is nearly full its contents are cooled to 15.5° , and made up to 100 c.c. with water at that temperature. If care be not taken to use small portions of water at a time during the washing, the filtrate may exceed 100 c.c. before the residue is perfectly free from soluble matter; in this case the solution must be evaporated to less than 100 c.c., and then made up to that bulk after cooling to 15.5° .

Treatment with ether frees the grain from fat, &c., alcohol of 0.90 sp.gr. removes the sugars, the proteids other than casein, &c., and water at 35° – 38° is intended to dissolve the amylans, &c., whilst the diastase is made to act on the residue at the temperature and under the conditions under which it dissolves starch. The 100 c.c. solution contains, therefore, the products of the transformation or decomposition of the substance.

The maltose present in it is now determined by means of Fehling's solution, and the dextrin calculated from the optical rotation. The maltose found multiplied by 1.055 gives the equivalent starch, and this added to the dextrin gives the total starch in the solution.

The methods of estimating starch in cereals

have been fully investigated in the Guinness Research Laboratory (Trans. Guinness Research Lab. 1903, 1, 79) under the direction of H. T. Brown, and a modification of O'Sullivan's method is recommended, in which the time required for the estimation is reduced to 5 hours. The details given are as follows: 5 grms. of the very finely ground grain are weighed out into a paper thimble and placed in the extraction apparatus, the moisture being determined on another portion of the ground material. The extractor recommended is essentially Soxhlet's form, but the wide vapour tube is connected with the top of the condenser tube so that the course of the condensed vapour is always downwards. The vessel for boiling the solvent is a thin round-bottomed Erlenmeyer flask, made of copper. The condenser has a second tube which affords additional condensing surface and also serves to keep the system under normal pressure. Eighty c.c. of alcohol of sp.gr. 0.920 are introduced into the copper flask, and the working of the apparatus adjusted so that the barley in the thimble is washed with alcohol of sp.gr. 0.900 for 3 hours (malt requires about 9 hours' washing, owing to the higher content of reducing sugars), when the whole of the reducing substances and alcohol-soluble nitrogen compounds are removed.

The contents of the thimble are now transferred to a beaker containing about 100 c.c. of water, and the whole thoroughly boiled. After cooling to 57° , 10 c.c. of an active malt-extract are added and the conversion is allowed to proceed for 60 mins. The solution is then boiled, filtered into a 200 c.c. flask, the residue well washed, and the volume adjusted after cooling. The cupric oxide reduction of the solution is determined and the maltose calculated, after correction for the reduction due to the malt extract.

In calculating the starch, the authors take advantage of the fact that when starch is hydrolysed by active diastase under suitable conditions, there is a well-defined resting stage which closely approximates to the 'No. 8 equation' of Brown and Heron (*l.c.*, p. 161), and which shows 100 parts of starch yielding 84.4 p.c. of maltose. The starch equivalent of the maltose determined in the solution is thus ascertained, on the assumption, if the conditions of the theoretical equation have been complied with, that 84.4 parts of maltose correspond to 100 parts of starch.

They summarise the chief precautions to be taken in carrying out this process as follows:—

It is necessary to grind the sample as fine as possible.

The extraction of the reducing substances with alcohol must not be less than 3 hours for barley and 7 hours for malt.

The converting power of the malt extract must always be determined with all possible accuracy and under the usual conditions. A malt should be chosen which has been dried on the kiln at 50° – 52° , and has a diastatic power of 80 Lintner.

A. R. Ling has further simplified the above method as applied to barley and wheat (*see J. Inst. of Brewing*, 1922, p. 838). His method is as follows:—

Estimation of starch in barley and wheat.—

It has been shown by H. T. Brown and G. H. Morris that when starch is hydrolysed by malt diastase under suitable conditions, an apparent resting stage is reached when 84.4 parts of maltose measured by the reducing power has been produced from 100 parts of anhydrous starch. This observation was made the basis of a method of estimating starch by H. T. Brown and his co-workers (Trans. Guinness Research Lab., 1903, 88), who showed that the amount of apparent maltose produced varies with the diastatic power of the malt used.

Ling, Price and Callow (Journ. Institute of Brewing, 1922, 838) have established the relation between the percentage of maltose obtained from barley or wheat starch. They find that both these starches give the same amount of apparent maltose under identical conditions. The results are plotted on the co-ordinate system, taking the diastatic powers on the Lintner scale as ordinates and the percentage of apparent maltose as abscissæ (see Fig. 33). The method in its final form is as follows:—

About 5 grms. of the finely-ground grain is accurately weighed out from a weighing bottle, by difference, into a paper thimble, which is then placed in a Soxhlet extractor and extracted with alcohol of sp.gr. 0.920 for 3-3½ hours. The alcohol which distils over has a sp. gr. of 0.900. The flask containing the alcohol is heated on a sand-bath. This extraction removed the sugars and fats, and also those proteins which are soluble in alcohol of the strength named. No starch can be detected in the alcoholic extracts.

After the extraction the thimble is allowed to drain for a few minutes, and the contents are washed into a beaker of 300 c.c. capacity with about 100 c.c. of distilled water. The starch is then gelatinised by boiling the contents of the beaker, with constant stirring, for 10 minutes, when, as a rule, gelatinisation is complete, and the steam no longer smells of alcohol.

The starch paste is now cooled to 57°C. and placed in a water bath at that temperature. Ten c.c. of the extract from a malt of known diastatic power is then added to the paste, and the hydrolysis is allowed to proceed at 57° for an hour, stirring with a glass rod at intervals of about 5 minutes. It is no advantage to employ an electric turbine for the stirring, which, indeed, can be more efficiently carried out by hand. The conversion liquid is then boiled and filtered into a 200 c.c. graduated flask. The insoluble matter, paleæ, &c., are washed thoroughly, and the filtrate and washings, after cooling, made up to 200 c.c. Of this solution, after well mixing, 30 c.c. is diluted to 100 c.c. and the diluted solution titrated against 10 c.c. of Fehling's solution.

The blank experiment (water and malt extract only), by which the conversion liquid is corrected for the reducing substances present

in the malt extract, is carried out in the same manner as the actual conversion, the filtrate and washings being made up to 20 c.c.

The percentage of starch is calculated by the formula $S = 94.73M'/M$, in which S is the percentage of starch in the sample, M is the percentage of apparent maltose produced from

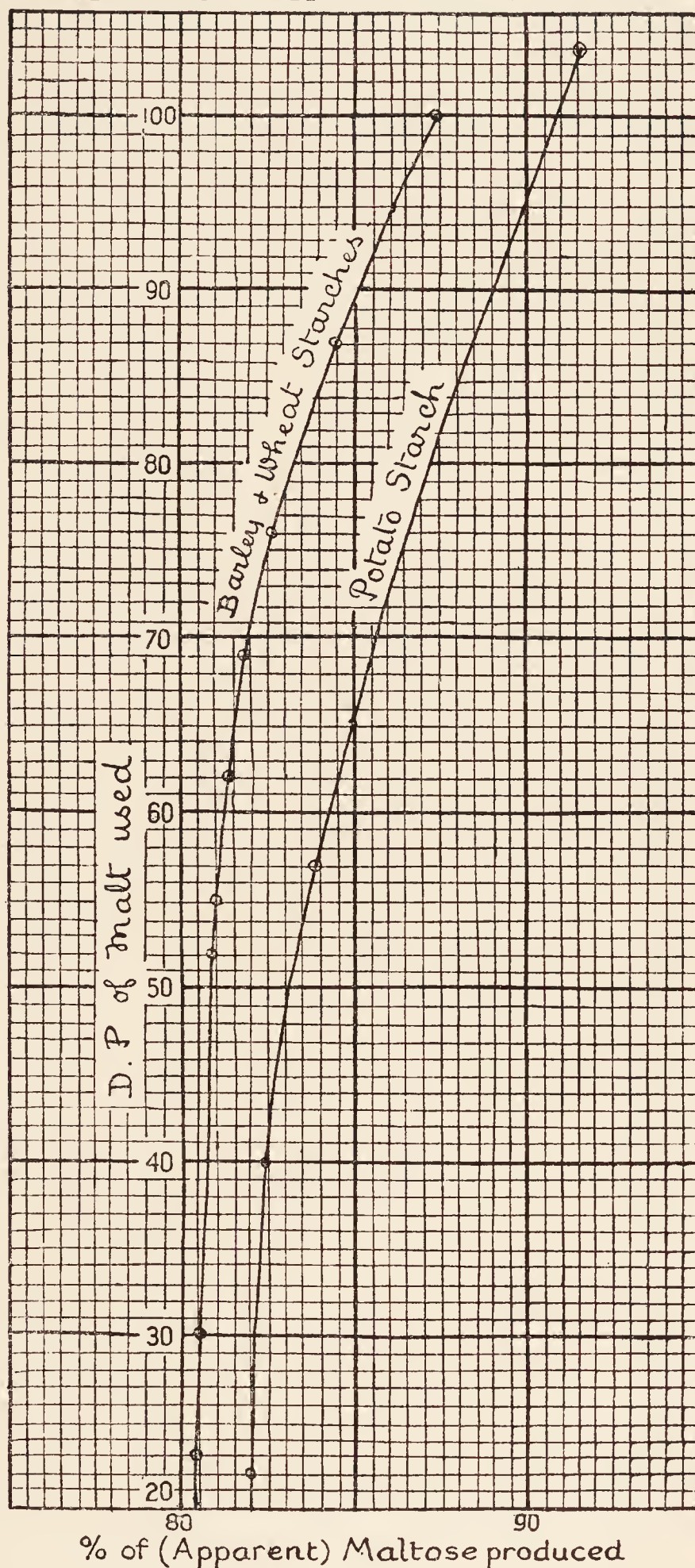


FIG. 33.

dry barley or wheat starch by the action of malt extract from malt of a definite diastatic power, under the conditions laid down (found on reference to curve), and M' is the percentage of apparent maltose produced from the sample under the same conditions and with malt of the same diastatic power.

A number of results are quoted showing that with barleys and wheats the percentages of starch found agree amongst themselves when malts of varying diastatic powers are employed in the analyses.

A further paper (No. III.) on this subject has been published by A. R. Ling, D. R. Nanji, and W. J. Harper (*J. Inst. Brewing*, 1924, 30, 838). They point out that in the previous method employing malt diastase, not only the amylopectin and amylose constituents of certain starches are hydrolysed, but also the major portion of the hemicellulose constituents when these are present. They suggest using barley diastase precipitated with alcohol (undried) (*see* Ling and Nanji, *Bio-Chem. J.* 1923, 593). The method is carried out as follows: 5 grms. of the finely ground barley or wheat is placed in a thimble and extracted in a Soxhlet apparatus with 50 p.c. alcohol for 3–4 hours. In this way the sugars and some of the proteins are removed. The extracted residue is then gelatinised with hot water in the ordinary manner, the paste cooled to 50°C., and 15 c.c. of freshly prepared barley extract (made by extracting 100 grms. of finely ground barley with 250°C. of water at the ordinary temperature), together with a few drops of toluene, added. The mixture is kept in a water bath at 50°C. for 12 hours, being stirred frequently during the first two hours. After this it is boiled, cooled, and made up to 500 c.c. at 15.5°C. The specific gravity and cupric reducing power of the filtrate are then determined.

Simultaneously with the barley or wheat conversion, a blank experiment is carried out with prime potato starch, in which the percentage of moisture has been determined. The potato starch is made into a paste and hydrolysed with the same barley extract or barley diastase solution as employed for the barley or wheat, and under precisely similar conditions. The percentage of maltose is then determined in this conversion liquid and expressed as a percentage on the dry starch, correction being made for the reducing power of the barley extract. This correction is obviated when precipitated barley diastase is employed.

Since potato starch contains nothing but amylose and amylopectin, the percentage of starch in the barley or wheat can be calculated by the following formula $\frac{100m}{m'}$, where m represents the maltose found in the barley or wheat conversion, expressed on 100 parts of the dry grain, and m' that found in the potato starch conversion expressed on 100 parts of the dry starch.

For the determination of maltose in the conversion they prefer the iodometric method as modified by Baker and Hulton (*Bio-Chem. J.*, 1920, 754; *Analyst*, 1921, 90) to the cupric reduction method. The results agree well with those obtained by the Fehling's volumetric method, the maximum differences being of the order of 1 p.c. of the total sugars.

Ling and Price suggest the following method for the estimation of starch in potatoes: A potato tuber is cleaned and peeled, and cut into very thin slices—about 8 grms. is accurately weighed out by difference into a clean glass mortar and pounded thoroughly to a pulp.

The pulp is extracted with 100 c.c. of water in a beaker during half an hour, with occasional stirring. The supernatant liquid is filtered, the extraction repeated as before, and the liquid filtered and the pulp and filter paper well washed with water. The filter and its contents are then transferred to the beaker containing the pulp and boiled for 10 mins. with 100 c.c. of water to gelatinise the starch. After cooling to 57°C., 10 c.c. of the extract of a malt of known diastatic power is added, and the hydrolysis allowed to proceed for one hour, after which the liquid is boiled, cooled, transferred to a 200 c.c. flask, and an aliquot portion titrated with Fehling's solution. The percentage of starch is calculated as in the case of barley and wheat, applying, however, the appropriate curve (*see* Fig. 33). Very concordant results are obtained by using malts of different diastatic powers (*J. Inst. Brewing*, 1923, 29, 732).

According to F. Tempus (*Naturprodukte*, 1923, 52, through *J. Soc. Chem. Ind.*, Oct. 19, 1923, 992 A.), in the estimation of starch in vegetable materials, the difficulties attending accuracy can be overcome by means of a preliminary heating with strong ammonia solution, which brings about disruption of the cell walls and facilitates the removal of sugars, dextrin, hemicelluloses, and fats. A dried sample of the material, not more than 2 grms., is finely powdered and warmed for three hours in a stoppered glass vessel at 40°–45°C. with 50 c.c. of 25 per cent. solution of ammonia. It is then filtered through a linen filter on a Gooch crucible, washed well, the residue finely ground, and the starch estimated by the diastase method.

For the estimation of starch in plant tissues, W. A. Davies uses taka-diastase, which converts starch into maltose and dextrose, thereby avoiding the loss of dextrin which occurs in the purification of the solution if O'Sullivan's method is used (*see* *J. Agri. Sci.*, 1914, vol. vi. part 2, and *J. Soc. Chem. Ind.* 1916, 35, 201).

Later work by Horton has shown that the method is not entirely trustworthy (*J. Agric. Sci.* 1921, part 2, p. 240).

The starch in potatoes is estimated in a rough-and-ready manner by ascertaining the specific gravity of the tuber. Five kilograms of potatoes freed from dirt are taken and weighed in water. The weight in water divided into the original weight in air gives the specific gravity. The specific gravity ranges from 1.08 to 1.15, the heaviest potatoes containing most starch and most dry matter. Tables have been drawn up by Behrend, Märcker, and Morgen for ascertaining the percentage of starch from the specific gravity of the potato tuber, which give results accurate within 2 p.c.

Several varieties of starch are largely used in the adulteration of cocoa and chocolate, sago being frequently employed for this purpose; but, owing to the variable amount of starch in cocoa beans, a chemical analysis of the supposed adulterated article cannot be regarded as decisive, unless the percentage of starch found amounts to more than 10 p.c. In such cases it is advisable to resort to microscopical examination, and for this purpose the chocolate is best deprived of its fat and sugar before being placed under the microscope. The following method

of examination is recommended by Hartwich (Chem. Zeit. 12, 375). The number of starch granules (which may be stained with iodine solution if advisable) in each field is counted, and a mean taken; a pure chocolate is then mixed with a corresponding amount of the supposed foreign starch, and examined in the same manner. In this way the quantity of starch added as an adulterant may be estimated with sufficient accuracy.

For estimation of starch in fodder, Leclerc (J. Pharm. Chim. [v.] 21, 641) gives the following method: 5 grms. of straw, hay, &c., are placed in a 250 c.c. flask, 10 c.c. of water added, and shaken until every particle of the substance under examination is thoroughly moistened. 180 c.c. of a neutral zinc chloride solution, sp.gr. 1.450, are next added, and the whole heated in a salt-water bath at 108° for 1½ hours. The flask is then taken out and cooled, and the volume made up with zinc chloride solution to 253 c.c. at normal temperature and filtered. From 25 c.c. to 100 c.c. of the filtrate is poured into a beaker containing 2 c.c. to 8 c.c. of hydrochloric acid and a sufficient quantity of 95 p.c. alcohol added to precipitate the whole of the dextrin and starch. After 24 hours the precipitate is collected on a tared filter and washed with 90 p.c. alcohol containing 0.5 p.c. hydrochloric acid until free from zinc chloride. The acid is then washed out with alcohol alone, and the precipitate weighed, then burnt, and the weight of the ash, of which there is usually a little, being carried down by the alcohol with the starch, deducted.

Starch is of very general occurrence in paper, and may be very easily detected by moistening the latter with a dilute solution of iodine, the intensity of the violet to blue coloration often forming the only means employed to ascertain the quantity of starch present. For its quantitative estimation Würster (Dingl. poly. J. 229, 538) proceeds as follows. The quantity of water present is first estimated, then the resin, by boiling out with alcohol, drying the paper, and weighing. The starch is next dissolved out by boiling the paper for some time with a mixture of equal parts of water and alcohol, to which a few drops of hydrochloric acid are added, and drying and weighing the residual paper; but, since the acid causes a certain loss in mineral constituents, the ash must be determined in the paper before and after extraction, and the difference deducted from the result. The following p.c. results were obtained by this method:—

Paper	Water	Resin	Starch	Ash	Fibre and cellulose by difference
Fine post, thin . . .	7.2	2.9	3.5	1.8	84.6
Fine post, medium . .	7.6	5.4	3.1	1.9	82.0
Fine post, strong . .	7.2	3.4	3.7	7.8	77.9
Common writing paper	5.8	3.9	9.1	33.4	47.8

For a colorimetric method for the estimation of starch, see Thomas (J. Amer. Chem. Soc. 1924, 46, 1670; Analyst, 1924, 49, 438). The

picric acid colorimetric method hitherto used in biological work (Analyst, 1921, 288, 598) may be applied to the estimation of starch or sugar in feeding stuffs and similar materials. In the case of starch, the preliminary hydrolysis cannot be effected by means of taka-diastrase, since concordant results are unobtainable in that way; if, however, a cold water extract of malt is used, the results are satisfactory. When reducing sugars are to be estimated, the colour is developed immediately the sodium carbonate is added to the solution. With sugars that require hydrolysis, however, advantage is taken of the hydrolysing properties of the picric acid, and the alkali is added only after the hydrolysis has taken place. When the starch or sugar is accompanied by mucilaginous substances such as are found in linseed cake, apple pomace, or pectin pulp, or by polyphenols, aldehydes, ketones, purine bases, the colouring matters present in molasses and the like, this colorimetric method yields high results; such disturbing substances may, however, often be eliminated by special preliminary treatment. The procedure to be followed in the case of starch and in that of sugars is given in detail. The advantages of the method are its applicability to small samples or to materials containing small proportions of starch or sugar, the saving of time in comparison with the copper reduction method, and the simplicity of the manipulation, preparation of crucibles and the handling of bulky solutions being avoided (M. R. Coe and G. L. Bidwell, J. Assoc. Off. Agric. Chem. 1924, 7, 297; Analyst, 1924, 49, 234). For the optical determination of starch in technical starch products and in parts of plants by means of the interferometer, see Wolff (Zeitsch. angew. Chem. 1924, 37, 206; Chem. Soc. Abstr. 1924, ii. 506).

The starch met with in commerce and used for laundry and manufacturing purposes is almost exclusively derived from rice, maize, and potatoes, and generally contains very little or no impurities. These, when they do occur, consist of vegetable fibre, gluten, or albuminoid matter, remains of pulp water, and other mineral matters. Fibre gets into the finished starch owing to imperfect arrangement of the sieves. Remains of pulp water in starch are owing to bad washing, whilst the presence of sand and other mineral matter may be due to the mixing of that portion of the starch which settles in the washing tanks next to the axis of the stirring apparatus, with the bulk of the starch—or to addition as an adulterant.

The quantity of mineral matter in starch should not exceed 0.5 p.c. When it is more than this, mineral matter, frequently barium or calcium sulphate, has been added; or the starch has been carelessly washed and not properly purified—in this case the other impurities will also be high.

As has already been stated, the proportion of moisture in ordinary air-dried starch averages about 18 p.c. It may be determined by drying the starch *in vacuo* over sulphuric acid, and finishing off in a current of dry air at 100°, the temperature being very gradually raised to this point. If the starch is at all acid, this must be neutralised by moistening it with a few drops of very dilute ammonia.

J. H. Hoffman (Woch. für Brauerei, 1903, 31) proposes a method in which the starchy matter is heated to drive out the water, which is collected and measured. Fifty grms of starch are immersed in 400 c.c. of oil of turpentine and 10 c.c. of toluene in a vessel and heated, first at 50°, then to 140°, and finally to 155°, for 5 minutes in each case. The water formed is collected and measured, a correction of 0.2 c.c. added and the whole multiplied by 2 to give the percentage of water in the starch.

For the estimation of water in potato starch, Saare (Chem. Zeit. 52, 934) has worked out a method which combines rapidity of execution with sufficient accuracy for technical purposes. 100 grms. of the starch are rinsed into a tared 250 c.c. flask, which is then filled up to the mark with water at 17.5° and weighed; the weight of the empty flask is now deducted from this, and the percentage of water corresponding to the difference found from the following table:—

Weight found	Water p.c.	Weight found	Water p.c.
289.40	0	277.20	31
289.00	1	276.80	32
288.60	2	276.40	33
288.20	3	276.00	34
287.80	4	275.60	35
287.40	5	275.20	36
287.05	6	274.80	37
286.65	7	274.40	38
286.25	8	274.05	39
285.85	9	273.65	40
285.45	10	273.25	41
285.05	11	272.85	42
284.65	12	272.45	43
284.25	13	272.05	44
283.90	14	271.70	45
283.50	15	271.30	46
283.10	16	270.90	47
282.70	17	280.50	48
282.30	18	270.10	49
281.90	19	269.70	50
281.50	20	269.30	51
281.10	21	268.90	52
280.75	22	268.50	53
280.35	23	268.10	54
279.95	24	267.75	55
279.55	25	267.35	56
279.15	26	266.95	57
278.75	27	266.55	58
278.35	28	266.15	59
278.00	29	265.75	60
277.60	30		

The results obtained are correct to 0.5 p.c. The method may also be applied to the estimation of the water in 'green' starch, and may be used for testing the progress of the drying process in the drying chambers.

The following rule may be employed in the place of the above table:—

From the weight of starch and water contained in the bottle subtract 250 and divide the difference by 0.3987, when the quotient will be the percentage of starch in the sample.

It may be more generally expressed:—

$$\frac{\text{contents of bottle in grms. minus capacity of bottle in c.c.}}{0.3987} = \text{grms. of anhydrous starch in weight of sample taken.}$$

MANUFACTURE AND PROPERTIES OF STARCH ESTERS.

Under the above title, the subject of starch esters is dealt with by J. Traquair (J. Soc. Chem. Ind. 1909, 288).

This article deals with starch nitrate, starch formate, and starch acetate; the last-mentioned under the name of 'feculose' is now used for a number of purposes, and is of particular interest.

It is marketed by Messrs. Wm. Wotherspoon, Ltd., Glenfield Starch Works, Paisley.

The following are extracts from J. Traquair's paper:

Starch nitrate.—This product has been known for many years, and its preparation and properties have been dealt with in various publications, one of which, 'Nitriung von Kohlenhydraten' (W. Will and P. Lenze, Berl. Ber. 1898, 68), may be mentioned. The product when thoroughly purified is quite stable, but as it is only of value as an explosive, it need not be further dealt with.

Starch formate.—Formic acid was first introduced on a commercial scale in 1902, and about the same time the first experiments were made to ascertain its action on starch. Formic acid swells starch in the cold, and if perfectly dry starch is mixed with 1½ to 2 times its weight of 99 p.c. formic acid it swells to a paste in 3 minutes. On warming on the water-bath for 15–20 minutes a clear, gummy solution is obtained, which can be drawn out into fine threads. On following the process with the microscope, the granules are seen to be only slightly swollen, but are transformed to a soft jelly, as they spread out under a cover glass. The clear solution, on pouring into cold water, is precipitated as a white flocculent mass. It is plastic at first, but on washing with water, forms a granular mass which is easily filtered and dried. The product is a white powder, but lacks the characteristic starch appearance; the yield is about 120 p.c. of the starch used.

Starch acetate.—Experiments were begun in 1901, and about the same time a paper on the acetylation of soluble starch, by F. Pregl, was published in the Monatsh. für Chemie, 1901, 22 (19), 1049–1066. Soluble starch prepared by Zulkowsky's method was treated at ordinary temperature for 48 hours with 10 times its weight of acetic anhydride containing 1 p.c. sulphuric acid. It yielded a tri-acetate on a C₆ formula. The product is insoluble in alcohol and water, gives no coloration with iodine, and does not reduce Fehling's solution. The yield was 132 p.c. of the starch, and saponification with potassium hydroxide regenerated 'soluble starch.'

When starch is treated with twice its weight of glacial acetic acid and kept at 60°C. for two days, the product is insoluble in cold water, and can be washed and dried like ordinary starch. When boiled at 1–10 it gives a paste

of the usual consistency, but which shows no tendency to revert on standing, *i.e.* the solution remains clear for months.

The present writer (in conjunction with Messrs. Cross and Bevan) has given some figures regarding the acetylation of starch by treatment with glacial acetic acid (*see* 'Die Niederen Acetyl-derivate von Stärke und Cellulose,' *Chemiker Zeitung*, 1905, 29, No. 39).

Acetic acid in aqueous solution has little action on starch, and no useful results were obtained. Glacial acetic acid has been found to be most suitable, and gives on the whole the best results from a technical point of view. It is necessary to use as nearly anhydrous materials as possible, and therefore the starch requires to be dried, so that it contains not more than 3 or 4 p.c. moisture. For commercial purposes, the reaction must be limited to a product insoluble in cold water, so that the excess of acid can be removed by washing by decantation. With excess of acid at 90°C. the limit is about 8 hours' treatment, and at 120°C. 2 to 3 hours. The product insoluble in water in each case showing a fixation of 4 to 5 p.c. acetic acid. The product, when swelled, with 5 or 6 times its weight of water, gives a clear viscous solution which is permanent, and on pouring out on a glass plate dries to a clear continuous film.

Technical development.—The process was patented in 1902 in Britain and several other countries, and in Germany a patent was granted after considerable opposition on the part of some local makers of 'soluble starch.'

The word 'feculose' (from 'fecula,' Latin for starch), was registered, and by this term the various commercial starch esters are now designated.

It has been found that the various commercial starches, *e.g.* potato, maize, rice, tapioca, sago, and wheat, give in some degree a product with distinct physical properties.

The larger granuled starches are preferred, owing to the ease with which they can be washed free of acid, but all are used more or less.

It is evident that by varying the starch base operated on, the reacting acids, the time and temperature of treatment, a range of products of endless variety can be obtained. No other reaction presents such a field of possibilities, and this is a strong point in favour of this type of reactions. It is possible to produce varieties of acetylated starch, giving solutions of varying consistencies from a thick jelly at 1–10 to a thin solution at 5–10; also types giving soft lustrous films on glass, and others stiff dull films.

Properties.—Feculose differs little in appearance from ordinary starch, and on boiling with water it gives a clear homogeneous solution which does not 'set' or revert on standing a few hours. The films obtained by allowing a little of the solution to dry on a clean glass plate are clear and flexible, and equal to those obtained from the finest gelatin. The solution does not reduce Fehling's solution, and gives the usual blue with iodine. It is precipitated by alcohol or strong solutions of certain salts in a similar way to ordinary soluble starch, and also readily reacts with diastase under the usual conditions.

Feculose is an ideal substitute for gelatin and vegetable gum in the manufacture of sweets,

and it is also largely used as a 'size' in paper-making.

Being a true colloid, it has obvious applications in the textile trade.

For the compounds of starch, *see* Bergmann and Ludewig (*Ber.* 1924, 57, [B] 961; *Chem. Soc Abstr.* 1924, 126, i. 837).

A. R. L., D. R. N.

STARCH GUM *v.* DEXTRIN.

STASSFURTITE *v.* BORACITE.

STAUROLITE. Basic aluminium ferrous-iron silicate, $\text{HFeAl}_5\text{Si}_2\text{O}_{13}$, crystallised in the orthorhombic system. Ferric-iron and magnesium replace aluminium and ferrous-iron respectively in small amount. The material is, however, often very impure, even crystals enclosing as much as 30–40 p.c. of quartz and other minerals. The crystals are usually twinned, giving rise to cross-like forms; hence the names *pierres de croix*, *lapis crucifer*, and staurolite, from *σταυρός*, cross, and *λίθος*, stone. The colour is dark reddish-brown and the material usually opaque; sp.gr. 3.65–3.77; $\text{H.}=7-7\frac{1}{2}$. Staurolite is a characteristic mineral of crystalline schists and metamorphic rocks; and by reason of its resistance to weathering processes it is often found as grains in sands. It is occasionally cut as a gem-stone, but only rarely is it found of sufficient transparency for this purpose. The twinned crosses are worn in their rough state as charms. L. J. S.

STAVESACRE SEEDS. *Staphisagriae semina*. The dried ripe seeds of *Delphinium Staphisagria*, Linn. *v.* DELPHININE.

STEAM. When water, by the agency of heat—or otherwise,—has so far changed its state as to become a compressible fluid, it is known as *steam*.

To produce steam for the purpose of performing work by its agency, water must be submitted to the action of heat until that temperature is reached at which the change from liquid to vapour is realised. This temperature, which is generally known as the 'boiling-point,' is variable, and dependent on external conditions; namely, the pressure on the surface of the liquid. At any particular pressure there is one temperature, and one only, at which steam and water can exist in equilibrium with one another.

In effecting this change of state a quantity of heat is absorbed without any rise of temperature. This is known as 'the latent heat of vaporisation,' or, more commonly, in the case of water, as 'the latent heat of steam.'

At 100° and 760 mm. pressure the quantity of heat absorbed in changing 1 grm. of water to 1 grm. of steam is 536.5 therms. As the pressure is increased, so the boiling-point rises, and the latent heat absorbed in the change diminishes. Values of the boiling-point and latent heat corresponding to temperatures are given in the 'steam table' quoted.

The following formulæ, showing the relations between temperature, pressure, and latent heat may be given, without going into the reasoning on which they are based, which is somewhat outside the scope of this article

(a) Regnault's formula—

$$L' = 606.5 - 0.695t$$

where L_t = latent heat at temperature t .

(β) The latent heat equation—

$$dT = \frac{T(v_2 - v_1)dp}{L \cdot J}$$

where L =latent heat; J =Joule's equivalent; v_2 =volume of 1 grm. of steam at temperature T ; v_1 =volume of 1 grm. of water at temperature T ; T =absolute temperature; dp =small increase in pressure (dynes); dT =corresponding change in temperature.

The pressure and boiling-point of a liquid cannot be raised indefinitely. If a quantity of water is heated in a sealed tube of strong glass, it is found that upon reaching a certain temperature the 'meniscus'—or surface differentiating the liquid from the vapour—disappears, and the contents of the tube become homogeneous. For water this temperature is 362° . Above this temperature steam *cannot* be converted into water, no matter how high the pressure to which it is subjected. This is known as the *critical temperature*.

The existence of such a temperature can be proved from theoretical considerations, and by the use of Van der Waal's equation—based upon the kinetic theory of gases—its value can be ascertained. Such proof, however, need not be considered here.

Entropy. The entropy is that function of the conditions of a body, such that, if it change from a value A to a value B , reversibly—

$$(B-A) = \int_A^B \frac{dH}{\theta}$$

Let a gram of water undergo a small increase of temperature dT at temperature T . Then heat absorbed $= \sigma dT$ (where σ =specific heat).

With water $\sigma=1$. Therefore heat absorbed $= dT$.

The temperature at which this heat is absorbed is T . Therefore increase in entropy $= \frac{dT}{T}$.

And change in entropy when the liquid is heated from T_2 to T_1

$$= \int_{T_2}^{T_1} \frac{dT}{T} = \log \frac{T_1}{T_2}$$

If $T_2=273^\circ$ abs. and entropy at this temperature is taken as zero, then entropy $= \log \frac{T_1}{273}$.

At the boiling-point of water under atmospheric pressure the entropy of 1 grm. of water $= \log \frac{373}{273}$.

Let this be converted into steam at the same temperature, the increase in entropy $= \frac{536.5}{373}$.

Therefore the entropy of 1 grm. of steam at $100^\circ = \log \frac{373}{273} + \frac{536.5}{373}$.

The 'θ-φ' diagram.—The relations between entropy and temperature as water is converted into steam may be represented in diagrammatic form. It is usual to take the values of the entropy as abscissæ and the values of the temperature as ordinates. The temperature is

represented by the symbol 'θ' and the entropy by 'φ.'

In this way two curves may be plotted. One the entropy curve for water and the other the entropy curve for steam. The *area*, included between such entropy-temperature curves representing a complete cycle, gives a measure of the *heat* put into the system and that taken out. Wherefore the entropy-temperature diagram is very useful as a means of obtaining absolute values of heat efficiencies.

The increase of entropy in the case of *superheated* steam is given by the formula—

$$\text{Increase in entropy} = \sigma \int_{T_2}^{T_1} \frac{dT}{T} = \sigma \log \frac{T_1}{T_2}$$

where σ =specific heat of superheated steam.

In all entropy-temperature diagrams, *adiabatic* changes are represented by vertical lines, since, during an adiabatic change the entropy is constant in value, *i.e.* the change is 'isentropic.' Isothermal changes are represented by horizontal lines.

Velocity of steam.—The velocity acquired by steam upon adiabatic expansion from a nozzle has become a matter of much importance owing to the development of the steam turbine. The velocity is obtained as follows:—

$$\text{The velocity, } v = \sqrt{2g \cdot J \cdot W} = 223.8 \sqrt{W}$$

where g =acceleration of gravity, J =Joule's equivalent, and W =work done. And the work done (in ft.-lbs.):

$$= J \left\{ (T_1 - T_2) \left(1 + \frac{L_1}{T_1} \right) - T_2 \log \frac{T_1}{T_2} \right\}$$

for initially dry steam, or

$$= J \left\{ (T_1 - T_2) \left(1 + \frac{x_1 L_1}{T_1} \right) - T_2 \log \frac{T_1}{T_2} \right\}$$

for wet steam, or

$$= J \left\{ (T_1 - T_2) \left(1 + \frac{L_1}{T_1} \right) - T_2 \log \frac{T_1}{T_2} + C_p (T_s - T_1) - C_p (\log T_s - \log T_1) T_2 \right\}$$

for superheated steam; where J =Joule's equivalent; T_1 =initial saturation temperature of steam (absolute); T_s =initial superheat temperature of steam (absolute); T_2 =final temperature of steam after expansion (absolute); L_1 =latent heat at temperature T_1 ; x_1 ='dryness' of the steam; C_p =specific heat of superheated steam at constant pressure.

The quantity of heat required to convert 1 lb. of water into steam, from an open vessel, or at atmospheric pressure, is 1146.1 units $-F^\circ$, as given in the third column of the table (p. 400) of the properties of saturated steam.

In a closed vessel, such as a steam boiler, the temperature at which steam is produced differs with different pressures (*see* Table, p. 400). The total quantity of heat required to convert 1 lb. of water into steam is very nearly the same at all pressures (*see* Table).

In Fig. 1 let A be the cylinder of a steam engine, and b the piston, and let the piston occupy the dotted position c . Now let steam at 40 lbs. pressure per square inch above the atmosphere, or 54.7 lbs. absolute ($40+14.7$), be ad-

mitted behind the piston, and let the admission be continued till the piston arrives at d ; then let the steam supply be stopped. The piston can then make no further movement except by virtue of the expansive force of the steam. Assume the piston to have moved to the position b , or four times as far from the end of the cylinder as the point d , where the steam supply was stopped; the steam in the cylinder will then have been expanded to four times its former volume.

Now if we select a scale on which the height from e to f represents 54·7 lbs., and make ei equal to 14·7 lbs., we shall then be able to complete the figure e, f, d, g, h, e , the area of which represents the total force exerted by the steam on the piston, the ordinates of the curve representing on the scale the pressures at the different points occupied by the piston in its movement.

We have assumed the steam to have now expanded to four times its former volume; its pressure will then be $\frac{54.7}{4} = 13.67$ lbs.

To find the pressure at any point between d and g , draw the line kd , parallel to ef and

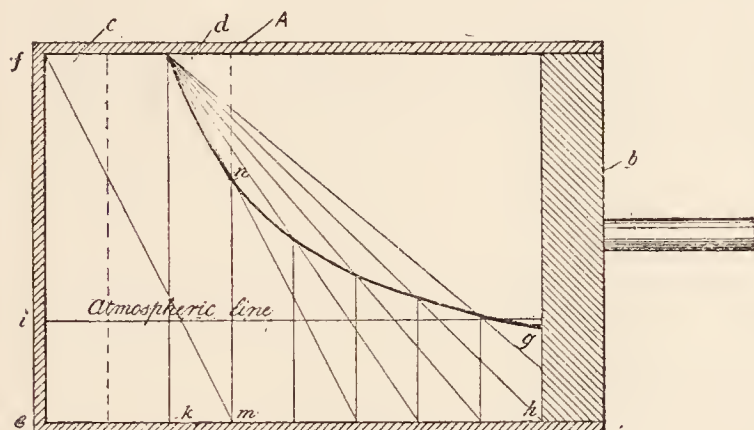


FIG. 1.

perpendicular to eh ; then take any point m , making mn parallel to kd ; join fm , and draw dn parallel to fm . The point n is a point in the curve of pressures, and mn represents on the scale the pressure of the steam when the piston was at that point. All other points in the curve dng can be determined in the same way.

The average pressure of the steam diagram, e, f, d, g, h, e may be calculated thus :

Let R = the ratio of expansion ; H , the hyperbolic log. of the number expressing that ratio ; p , the initial pressure of the steam ; p , the mean pressure—then

$$p = P \frac{1 + H}{R}$$

Taking the example before us

$$R = 4, \quad H = 1.386, \quad P = 54.7$$

then $54.7 \frac{1 + 1.386}{4} = 3.26$ lbs. mean pressure.

We have assumed that the pressure of steam has been fully utilised down to the line e , h , or line of no pressure or perfect vacuum. In practice this is not realised, and the bottom line of the actual steam diagram is generally 2 lbs. above that of a perfect vacuum; the real mean pressure would therefore be not 32·6 lbs., but 30·6 lbs. We have assumed the expansion to be isothermal. It is not so, and the practical effect of the conducting power of the cylinder is, that during the former part of the stroke

of the piston, steam is being condensed in the cylinder, and during the latter part it is being re-evaporated.

Steam diagrams.

We get our knowledge of what actually takes place in a steam-engine cylinder from the indicator. This instrument is illustrated by Fig. 2. It consists of a drum *a* (on which is

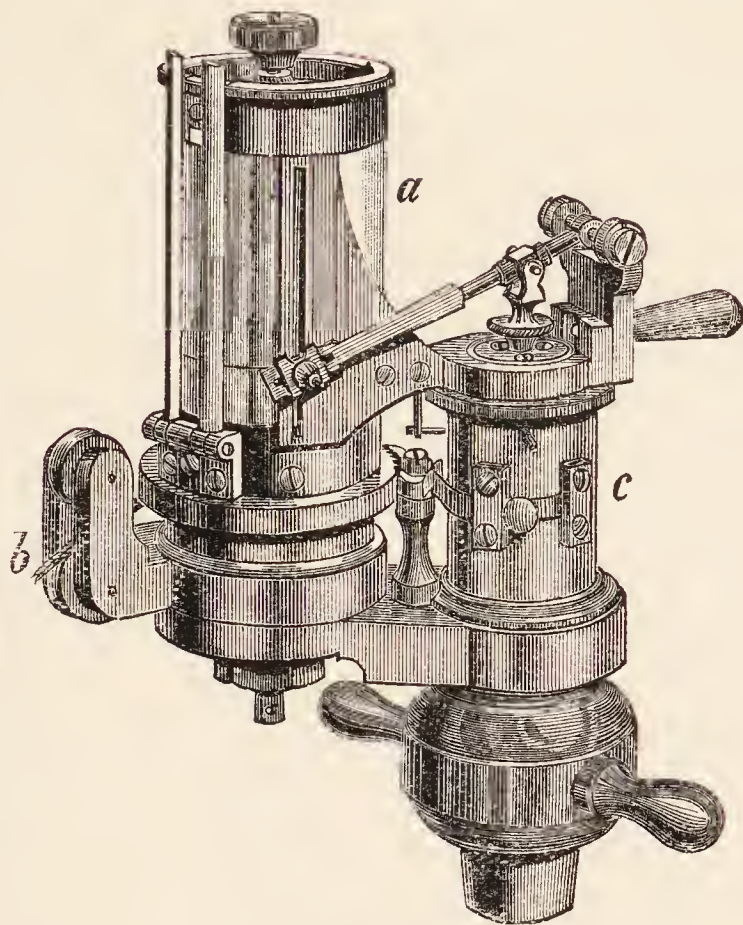


FIG. 2.

fastened a sheet of paper) made to oscillate backward and forward on its axis by means of a cord connection *b* to a moving part of the engine, having the motion of the piston on a reduced scale. At the side of the drum is placed a small cylinder *c* having a piston held down against the seam pressure by a spring of known tension. Let the piston be 1 square in. in area, and the tension of the spring 30 lbs. to the inch ; then a

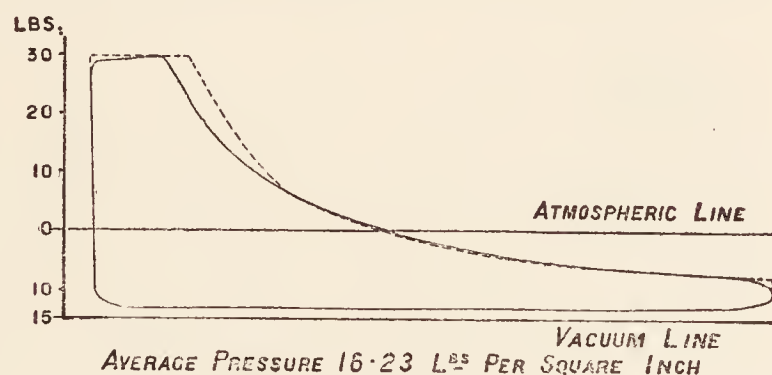


FIG. 3.

pencil attached to the piston would indicate by its position the pressure of steam on the piston, at a scale of 30 lbs. per square inch.

The pencil is made to mark a horizontal line on the paper before the steam is turned on to the indicator piston ; that line is termed the atmospheric line, as it indicates the pressure of the atmosphere. The indicator being attached to one end of a steam cylinder by means of a pipe, and the drum being made to turn by the engine, the pencil is caused to describe a figure on the paper of the drum like that on Fig. 3, in which

the horizontal length represents the stroke of the engine on a reduced scale, and the vertical height the pressure of steam in the eylinder at all parts of the engine stroke. It is evident that the area of the figure represents the total force exerted behind the engine piston, and the average height of the diagram the average pressure of steam during that stroke. The average height—or, in other words, the average pressure—is obtained by the ordinary method of measuring irregular figures.

Fig. 3 represents an actual indicator diagram.

One horse-power equals 33,000 ft.-lbs. per

minute. Steam engines are of various types. Single eylinder in which the steam is expanded in one eylinder only, compound engines with two, and triple expansion engines with three cylinders. The modern triple engine receives steam at 150–200 lbs. pressure per square inch, and expands it to about 6 lbs.

The best examples of steam boilers give a heat efficiency of from 70 to 80 p.e., and evaporate from 9 to 11 lbs. of water per lb. of good coal. The combined heat efficiency of engine and boiler is from 15 to 20 p.c. in the best examples of condensing engines, with super-heated steam.

PROPERTIES OF SATURATED STEAM.

Total pressure per sq. in.	Temperature in Fahr. degrees	Total heat, in Fahr. degrees from water at 32°F.	Latent heat, Fahr. degrees	Density, or weight of one cubic foot	Volume of one pound of steam	Relative volume, or cubic feet of steam from one cubic foot of water
lbs.	Fahr°.	Fahr°.	Fahr°.	lbs.	Cubic feet	Rel. vol.
1	102·1	1113·1	1044·7	0·0030	330·36	20,600
5	162·3	1131·5	1001·5	0·0138	72·66	4,530
10	193·3	1140·9	978·2	0·0264	37·84	2,360
14·7 ¹	212·0	1146·6	965·8	0·0380	26·36	1,642
20	228·0	1151·5	954·3	0·0507	19·72	1,229
25	240·1	1155·2	945·6	0·0625	15·99	996
30	250·4	1158·3	938·2	0·0743	13·46	838
35	259·3	1161·0	931·9	0·0858	11·65	726
40	267·3	1163·5	926·2	0·0974	10·27	640
45	274·4	1165·6	921·0	0·1089	9·18	572
50	281·0	1167·6	916·3	0·1202	8·31	518
55	287·1	1169·5	911·9	0·1314	7·61	474
60	292·7	1171·2	907·9	0·1425	7·01	437
65	298·0	1172·8	904·1	0·1538	6·49	405
70	302·9	1174·3	900·6	0·1648	6·07	378
75	307·5	1175·7	897·3	0·1759	5·68	353
80	313·0	1177·1	894·0	0·1869	5·35	333
85	316·1	1178·3	891·1	0·1980	5·05	314
90	320·2	1179·6	888·1	0·2089	4·79	298
95	324·1	1180·8	885·3	0·2198	4·55	283
100	327·9	1181·9	882·6	0·2307	4·33	270

¹ Atmospheric pressure.

H. D.

STEARIC ACID, STEARIN v. OILS, FIXED, AND FATS.

According to E. Zerner (Naturprodukte, 1923, 83–94), the higher fatty acids and related compounds are slowly oxidised by air or oxygen at 130°C. in presenee of manganese stearate. The oxidation is accompanied by a rise in the acid and saponification values and, in the ease of an unsaturated compound such as oleic acid, by a fall in the iodine value. When stearic acid was oxidised in this manner for 31 hours, the residue obtained formed a soap which lathered well, but could not be salted out, indicating the formation of hydroxy acids. It contained unsaponifiable matter, apparently an alcohol of the formula C₁₄H₃₀O, and in it sueinie, pimelic, and œnanthic acids were detected. The distillate carried forward by the current of air during oxidation contained the lower fatty acids down to formic acid, and an alcohol C₁₂H₂₆O. Oleic acid when oxidised in the same way gave a varnish-like residue which did not dry. When ethyl stearate was oxidised there

was no evidence, from the rate of disappearance of the ethoxy group, that either end of the chain was attacked preferentially. Compounds containing less than eight carbon atoms in the chain are not oxidised (J. Soc. Chem. Ind. 1923, 42, 987 A).

The double melting-point of tristearin is attributed to the existence of two modifications, the more stable of which has m.p. 71·6–72·2°, and the unstable form about 55°, the latter being reconverted into the stable form on heating it at a higher temperature or allowing it to remain. In spite of the speed of solidification, the solidification point of tristearin is usually given as that of the unstable form (about 55°). The solidification point of pure tristearin was determined by the rise of temperature in Dalican’s method. It first showed signs of solidification at 53·8°; the temperature then rose normally to about 63·5°, remained almost constant for some time, and then rose rapidly to the maximum at about 69°. On ‘seeding’ liquid tristearin with the stable

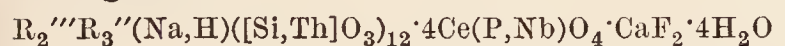
modification above 60°, solidification takes place without the formation of the unstable form, but the latter is apparently always produced after seeding, even with the stable form, at temperatures below 56°. Double solidification points are not necessarily shown by all the triglycerides which show a double melting-point. It appears to be an essential condition that the solidification of the unstable form shall produce sufficient heat to reach the temperature of transition into the stable form. The phenomenon was shown by hydrogenated soya-bean oil, but not by hydrogenated linseed or cotton-seed oil. The solidification point of hydrogenated linseed oil (65·9°) was not raised by 'seeding' (Nicolet, *J. Ind. Eng. Chem.* 1920, 12, 741-743; *Journ. Chem. Soc. Abstracts*, 1920 (October), i. 660).

STEAROSAN. Trade name for a compound of santalol and stearic acid.

STEATITE. (*Speckstein*, Ger.) A compact form of the mineral talc (*q.v.*).

STEEL *v.* IRON. For the specific and latent heats of iron and steel, see Mallock (*Nature*, 113, p. 566, April 19, 1924; *Sci. Abstr.* 1924, 27, 748).

STEENSTRUPINE. Hydrated silicate of cerium earths (Ce_2O_3 , &c., 28-36 p.c.), with thorium (ThO_2 , 2-7 p.c.), phosphorus (P_2O_5 , 4-8 p.c.), &c. The following formula has been given:—



where $\text{R}''' = \text{La, Di, Y, Fe}$, and $\text{R}'' = \text{Mn, Ca, Mg}$. Crystals are rhombohedral with an octahedral or tabular habit, a dark brown to nearly black colour, and a resinous lustre. Sp.gr. 3·38-3·47 (3·19 for massive material); $\text{H.} = 4-5$; decomposed by hydrochloric acid giving a dark brown solution which evolves chlorine. Well-developed isolated crystals 1-3 cm. across are somewhat abundant in the nepheline- and sodalite-syenites at several places in the Julianehaab district in south-west Greenland. L. J. S.

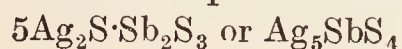
STELLITE. The name given to an alloy, or group of alloys, used for high-speed cutting tools, consisting essentially of cobalt and chromium with additions of tungsten, molybdenum, or both. Has a colour between that of steel and silver, is unchanged by dry or moist air below a dull red heat. Very hard and resistant to abrasion, cannot be forged as it retains its hardness at a full red heat, and can only be reduced to the desired form by casting and grinding to a cutting edge (Haynes, *Amer. Inst. of Metals*, 1915; *J. Soc. Chem. Ind.* 1915, 1058).

It is prepared by melting its components together in electric tilting furnaces of the arc type, in which the lower electrode is in contact with the metal bath. Current at 50 volts is employed at starting; and when the furnace is running smoothly, the voltage is increased to 100, the average ampèreage being about 80. The charge is poured at about 1550° into graphite moulds and the bars or shapes are first trimmed and then ground on alundum and carborundum wheels.

For cutting tools the alloy is made in three grades of hardness; a special grade has been employed for boring cylinders used in acro-

planes. Stellite is largely employed in the manufacture of automobiles and a malleable form, of modified composition, is used for making cutlery, surgical instruments, &c. (Wright, *Trans. Canadian Min. Inst.* 1918, 21, 272; *J. Soc. Chem. Ind.* 1919, 326, A).

STEPHANITE, 'black silver-ore,' or 'brittle silver-ore.' A silver sulphantimonite



occasionally mined as an ore of silver (Ag, 68·5 p.c.). Crystals are orthorhombic with an iron-black colour and brilliant metallic lustre. Considerable quantities of the massive mineral have been obtained from the Comstock lode in Nevada. L. J. S.

STETHAL. See *Spermaceti*, art. WAXES.

STIBICONITE $\text{Sb}_2\text{O}_4 \cdot \text{H}_2\text{O}$ *v.* ANTIMONY.

STIBIOTANTALITE. Antimony tantalate and columbate, $\text{Sb}_2\text{O}_3 \cdot (\text{Ta,Cb})_2\text{O}_5$, crystallised in the orthorhombic system with hemimorphic development. The formula has also been written in the form $\text{Sb}(\text{Ta,Cb})\text{O}_4$, showing a relation to pucherite (BiVO_4); and as $(\text{SbO})_2(\text{Ta,Cb})\text{O}_{2.8}$, similar to that of columbite. Analyses I.-III. of material from California; IV. from Australia (also NiO 0·08, H_2O 0·08):

	I.	II.	III.	IV.
Ta_2O_5 . .	13·00	33·86	41·92	51·13
Cb_2O_5 . .	37·30	21·47	16·19	7·56
Sb_2O_3 . .	49·28	44·26	40·95	40·23
Bi_2O_3 . .	0·53	0·33	0·60	0·82
	100·11	99·92	99·66	99·90
Sp.gr. . .	5·98	6·72	6·80	7·37

The mineral was first found in 1893 in the tin-bearing sands at Greenbushes in Western Australia, where it occurs as reddish- or greenish-yellow, water-worn grains, or sometimes attached to nodules of tantalite. Later, well-developed crystals were found with rubellite, lepidolite, &c., in pegmatite-veins in the gem mines at Mesa Grande in San Diego Co., California. The lustre is adamantine to resinous; $\text{H.} = 5-5\frac{1}{2}$; readily soluble in hydrofluoric acid. L. J. S.

STIBNITE, *Antimonite* or *Antimony-glance*. Native antimony sulphide (Sb_2S_3), of importance as an ore of antimony. It forms blade-like or acicular, orthorhombic crystals which possess a highly perfect cleavage in one plane direction parallel to their length. Radially-fibrous and lamellar masses, with the perfect cleavage conspicuous on their broken surfaces, are of common occurrence. Sp.gr. 4·6. The colour is steel-grey with a brilliant metallic lustre, but on exposure to light the surface becomes dulled. Although often regarded as a typically opaque mineral, very thin cleavage flakes of stibnite transmit a small amount of red light (refractive indices, $\alpha = 3·194$, $\beta = 4·046$, $\gamma = 4·303$ for wave-length 760), and they are still more transparent for heat rays (A. Hutchinson, *Min. Mag.* 1903, 13, 342; 1907, 14, 199). Light has a remarkable effect on the electrical conductivity of crystals of stibnite: the close proximity of a strong electric arc-light causes this to increase by over 200 p.c., and when the light is removed it quickly returns to its former value (F. M. Jaeger, *Zeitsch. Kryst. Min.* 1907, 44, 45).

The mineral is quite soft ($H.=2$), and the crystals are readily bent, with the production of characteristic zigzag forms. The bending is accompanied by a slipping, along a glide-plane, of one portion of the crystal over another portion. This gives rise to fine striations running transversely across the cleavage surfaces, which being almost always present (no doubt as a result of earth pressures) render stibnite a mineral easily recognisable at a glance.

Stibnite occurs in metalliferous veins, and is found at many localities. The finest specimens (magnificent groups of brilliant, prismatic crystals reaching a length of 20 ins.) come from the Ichinokawa antimony mine, near Saijo on the Japanese island of Shikoku. Good crystals, often penetrating crystals of barytes, are well known from Felsöbánya in Hungary. As an ore of antimony stibnite is mined in several countries, the principal ones, arranged in the order of their production, being: France (Auvergne), China (prov. Hunan), Italy, Bolivia, Mexico, Victoria, and Hungary.

Besides being smelted as an ore of antimony, stibnite is used to a limited extent for the preparation of pure hydrogen sulphide. In the East, powdered stibnite is employed for darkening the eyebrows, and it was also used by the ancients for the same purpose, hence the old name *platyophthalmon* for this mineral.

The atomic weight of antimony obtained from stibnite from various sources is found to vary considerably, thus:

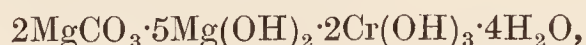
Hungarian material	Sb=121.144 (7 expts.)
Borneo material	Sb=121.563 (7 expts.)
Peruvian material	Sb=121.720 (7 expts.)
Bolivian material	Sb=122.374 (11 expts.)

The experimental results in each set of determinations are remarkably concordant, and appear to indicate that the distribution of the isotopes of antimony in the various stibnites is different (S. D. Muzaffar, J. Amer. Chem. Soc. 1923, 45, 2009–2013; J. Soc. Chem. Ind. 1923, 42, 1134 A).

Reaction between excess of metallic copper and stibnite begins at 500° and occurs readily at 600° – 700° , yielding a compound $3Cu_2S, Sb_2S_3$. At temperatures above 700° , this compound dissociates into antimony sulphide, which sublimes, and a residue of cuprous sulphide, which may thus conveniently be prepared (G. Marchal, Bull. Soc. chim. 1923, [iv.] 33, 597).

Reference.—Chung Yu Wang, Antimony, its History, Chemistry, Mineralogy, &c., London, 1909; Antimony, Imp. Min. Res. Bur. London, 1921, 1924. L. J. S.

STICHTITE. A hydrated basic carbonate of magnesium and chromium,



containing Cr_2O_3 20.6 p.c. It forms foliated masses with a pearly micaceous cleavage and a vivid lilac colour, in striking contrast with the bright green serpentine with which it is intimately associated. In appearance it is very like kämmererite (a chrome-chlorite containing Cr_2O_3 5–8 p.c.), for which indeed it had, until analysed, been mistaken. On the weathered surface it is dull brown, and then not easily recognised. Sp.gr. 2.16; $H.=1\frac{3}{4}$; optically uniaxial; soluble in hydrochloric acid to a

bright green solution. It occurs as patches and veins in serpentine, and as scales is often grouped with a radial arrangement around grains of chromite embedded in the serpentine. The mineral is thus clearly a secondary alteration product of chromite and serpentine. It is found, apparently in some abundance, on the serpentine ridge above the Adelaide mine near Dundas, on the west coast of Tasmania. This silver-lead mine is well known as yielding striking specimens of another chromium mineral, namely, splendid bright-red crystals of crocoite ($PbCrO_4$). Other occurrences of stichtite are in serpentine at Black Lake in Quebec and Barberton in Transvaal. The refractory chromite (*q.v.*) is the only common mineral containing chromium in large amount, and at present the sole source of this element. The readily soluble stichtite, if found in sufficiently large quantity, might therefore be of commercial importance. On account of its analogy in composition (containing chromium in place of ferric iron), and probably also in crystalline form, with the Italian mineral brugnatellite, stichtite has also been called chrome-brugnatellite (Rec. Geol. Survey, Tasmania, 1914, No. 2). L. J. S.

STICK LAC *v.* *Lac resin*, art. RESINS.

STICTAIC ACID, $C_{19}H_{14}O_9$, an acid found in *Sticta pulmonaria*, and probably identical with *stereocaulic acid*, obtained from various species of *stereocaulon*. White needles, becoming brown at 240° and decomposing at about 260° . Its alcoholic solution gives a deep violet-red coloration with ferric chloride; no coloration with calcium hypochlorite (Bargellini and Moncada, Gazzetta, 1921, 51, [ii.] 173). V. LICHENS.

STIGMASTEROL *v.* ORDEAL BEAN.

STILBENE, *toluylene*, *sym-diphenylethylene* $C_6H_5 \cdot CH:CH \cdot C_6H_5$, is formed when benzylidene chloride is heated with sodium (Limpricht, Annalen, 1866, 139, 38); by heating benzoin with zinc-dust and acetic acid (Blank, *ibid.* 1888, 248, 7); by the slow distillation of phenyl fumarate (Anschütz, Ber. 1885, 18, 1948); by the action of light on the silver salt of phenyl-nitromethane (Angeli, Castellana and Ferero, Chem. Zentr. 1909, [ii.] 975); on treating phenylbenzylcarbinol with dilute sulphuric acid; by heating a mixture of benzaldehyde and phenylacetic acid in a sealed tube—all of which methods indicate the above constitution.

Symmetrical stilbenes may be prepared by the interaction of magnesium aryl haloids and chloro- or bromo-acetal at 110° – 130° , and subsequent hydrolysis of the resulting α -ethoxy- $\alpha\beta$ -diarylethanes with dilute sulphuric acid. The preparation of stilbenes, both symmetrical and unsymmetrical may also be effected by the action of magnesium aryl haloids on chloro-acetaldehyde (Späth, Monatsh. 1914, 35, 463).

Preparation.—Stilbene is obtained in fair yields by dropping toluene into a red-hot tube containing lead oxide (Lorenz, Ber. 1874, 7, 1096); by heating benzthioaldehyde with copper powder (Klinger, *ibid.* 1877, 10, 1878), or more simply by heating benzaldehyde alone with sulphur in sealed tubes to 180° . Better results are obtained by treating deoxybenzoin with sodium ethoxide (Sudborough, Chem. Soc. Trans. 1895, 67, 604); by acting upon benzaldehyde with phenyl magnesium iodide (Klages and Heilmann, Ber. 1904, 37, 453); by the action of 10 p.c.

caustic soda on phenylnitromethane at a temperature of 160°, when a 90 p.c. yield is obtained (Wislicenus and Endies, *ibid.* 1903, 36, 1194).

Properties and reactions.—Monoclinic tables, m.p. 124°, b.p. 306°, insoluble in water, easily soluble in hot alcohol, ether, benzene, &c. Forms a disodium compound when shaken in ethereal solution with metallic sodium. In light of short wave-length stilbene undergoes auto-oxidation and in ultra-violet light isomerization (Stobbe, J. pr. Chem. 1914, [ii.] 90, 551). On passing through a heated tube it forms toluene and phenanthrene (Graebe, *ibid.* 1873, 6, 126); on reduction with hydriodic acid it yields dibenzyl; it is oxidised by chromic anhydride to benzoic acid; heated with sulphur it forms tetraphenylthiophen; by the action of sulphuric acid it forms a disulphonic acid (Limpricht and Schwanert, *Annalen*, 1868, 145, 335); it is converted by ozone into an ozonide (Harries, Ber. 1903, 36, 1933); on passing nitrogen peroxide into its benzene solution it forms stilbene nitrite (Gabriel, *ibid.* 1885, 18, 2438); with picric acid it forms an insoluble picrate, brown needles, m.p. 94°–95°; by the addition of bromine in carbon disulphide solution there are produced two stereoisomeric stilbene bromides (m.p. 237° and 110°) (Wislicenus and Seeler, *ibid.* 1895, 28, 2694).

With chlorine in ethereal solution it gives a mixture of α and β isomeric chlorides; the α -chloride, needles, m.p. 191°–193°, resists the action of pyridine even at 200°, whereas the β -chloride, m.p. 93°–94° gives *monochlorostilbene*, prismatic needles, m.p. 52°–54° (Pfeiffer, Ber. 1912, 45, 1810).

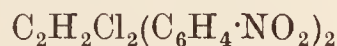
iso-Stilbene.—From the lower melting-point stilbene bromide obtained as above, a stereoisomeric modification of stilbene may be obtained by careful reduction. As this bromide has the trans-configuration *isostilbene* must be the trans-isomeride. It is extremely unstable, and on distillation, or under the influence of sunlight, or in presence of traces of bromine or iodine it passes immediately into ordinary stilbene, which consequently possesses the cis-configuration (Wislicenus, Chem. Zentr. 1901, [i.] 463).

***o*-Dinitrostilbene** from *o*-nitrobenzyl chloride and alcoholic potash, exists in two stereoisomeric forms (m.p. 126° and 196°); on reduction they yield the same *o*-diaminostilbene (Bischoff, Ber. 1888, 21, 2072).

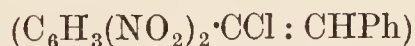
2 : 2'-Dinitrostilbene chloride



yellow needles, m.p. 152°–153°. Heated with pyridine at 160°–170° gives α -chloro-2 : 2'-dinitrostilbene, yellow needles, m.p. 124°; 4 : 4'-Dinitrostilbene dichloride



yellow crystals, m.p. 302°; 2 : 4-Dinitrostilbene gives two isomeric additive compounds with chlorine; the α -chloride (yellow leaflets, m.p. 167°) is obtained by the action of chlorine on the chloroform solution, whilst the β -chloride is the main product in carbon disulphide. When heated in pyridine both chlorides yield α -chloro-2 : 4-dinitrostilbene



prismatic needles, m.p. 104°, becoming red on

exposure to light. α -2 : 4-dinitrostilbene bromide, colourless needles, m.p. 185°; β -isomeride, pale yellow leaflets, m.p. 145°–146°, reddened by light (Pfeiffer, Ber. 1912, 45, 1810).

p-Hydroxystilbene



colourless crystalline powder, m.p. 184.5° (uncorr.); *p*-methoxystilbene, m.p. 136°. *p*-nitro-*p*'-methoxystilbene



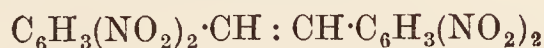
orange needles, m.p. 162° (uncorr.) (Hewitt, Lewcock and Pope, Chem. Soc. Trans. 101, 604).

p-Dinitrostilbene, prepared in the same way, has also been isolated in two forms (m.p. 210° and 280°), which form on reduction *p*-diaminostilbene (m.p. 227°) (Strakosch, Ber. 1873, 6, 328; Walden and Kernbaum, *ibid.* 1890, 23, 1959).

Di-p-chlorostilbene, leaflets, m.p. 177° (Späth, Monatsh. 1914, 35, 463).

Tetranitrostilbene, from tetranitrobenzyl chloride and alkali (m.p. 264°) (Kraususký, J. Russ. Phys. Chem. Soc. 27, 339).

2 : 6 : 2' : 6'-tetranitrostilbene



prepared by the action of alcoholic potassium hydroxide on dinitrobenzylbromide; faintly yellow needles (m.p. 250°) (Reich, Welter and Widmer, Ber. 1912, 45, 3055) (*cf.* Stoermer and Oehlert, Ber. 1922, 55 [B] 1232).

Nitrostilbene sulphonic acids (*v.* Bender, Ber. 1895, 28, 422; Fischer and Hepp, *ibid.* 1895, 28, 2281; Green and Wahl, *ibid.* 1897 30, 3100).

Stilbene colouring matters. *p*-Nitrotoluene and its *o*-substituted derivatives under the influence of alkalis yield derivatives of stilbene, which are the parent substances of numerous dyes (*see* AZO-COLOURING MATTERS).

STILPNOCHLORANE, STILPNOMELANE *v.* THURINGITE.

STIRLINGIA LATIFOLIA, ESSENTIAL OIL OF. In 1918 a sample of this oil examined at the Imperial Institute was found to consist almost entirely of acetophenone, which has remarkable soporific properties, and is employed in medicine under the name of 'Hypnone.' Hitherto all supplies of acetophenone have been prepared synthetically, the only previous record of its occurrence in a natural oil being in the oil of gum labdanum. *Stirlingia latifolia* is a small shrubby plant, which occurs abundantly in the coastal plains of Western Australia, so that ample supplies could be obtained. The yield of oil on distilling fresh plants with steam is 0.75 p.c., whilst young shoots gave a yield of 1.0 p.c. The best results are obtained from material gathered during the period of April to July. The oil received at the Imperial Institute was found to have the following constants compared with those of acetophenone :

	<i>Stirlingia latifolia</i> oil	Acetophenone
Sp.gr. at 15°C.	1.0310	1.0329
Boiling-point	195°–205°C.	202°C.
Optical rotation	+0.2°	inactive

The oil furnished a large yield of acetophenone-oxime (m.p. 58°–59°C.). A supply of dried stems and leaves of the plant subsequently

examined was found to have the following constants compared with the fresh sample:—

	Present sample	Previous sample of oil
Sp.gr. at 15/15°C.	1.0256	1.0310
Boiling-point	199°–205°C. (mostly 202°–203°)	195°–205°C.
Optical rotation	nil	+0.2°

The odour of the present sample was less pleasant than that of the oil distilled from the fresh plant in Australia, and as the yield of oil from the dried plant was very low it appears that oil was lost during the drying of the plant. Besides its use in medicine as a hypnotic, acetophenone has been used in soap perfumery, and is stated to blend well with terpineol, coumarin, heliotropin, and for this reason *Stirlingia* oil would probably find a market in place of pure acetophenone. As, however, the plant only yields 0.75 p.c. of oil it hardly seems likely that it will be profitable to collect and distil it on a commercial scale (Bull. Imp. Inst. No. 2, vol. xxi. 1923; J. Soc. Chem. Ind. 1924, 43, 68).

STIZOLOBIN, the globulin of the Chinese velvet bean, *Stizolobium niveum*, has the percentage composition C 53.03, H 7.05, N 16.33, S 0.65, and O 22.94. It contains about 1.35 p.c. cystein, 6.7 arginine, 2.4 histidine, and 8.5 p.c. lysine (Johns and Finks, J. Biol. Chem. 1918, 34, 429).

STOCKHOLM TAR. A bituminous liquid obtained from the wood of *Pinus sylvestris* (Linn.) and other species of *Pinus* by destructive distillation.

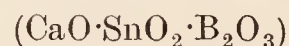
The tar exported from Stockholm in earlier times, and to which the term Stockholm tar was applied, was brought from the northern part of Sweden and from Finland, where the tar was produced by peasants from dry wood stumps burned in 'tjärdålar,' or specially made tar-burning ground. On arrival at the Stockholm tar court all barrels were 'wrecked' before being shipped abroad. The procedure of wrecking was as follows: After the barrel had been filled with tar it was left standing for some hours, when the water which had accumulated on the surface was drawn off and the barrel refilled with tar. The 'wreckers,' who were sworn servants of the Tjärhof, issued a certificate, which at that time was required for the export, stating that the barrels contained the regulation quantity and that the tar had been 'wrecked.' The old Stockholm tar was shipped in barrels of 125 litres. Several tar exporters in the north of Sweden still use barrels which have been examined by the State Comptrollers as to their capacity, and if found to hold the right measure the barrel is stamped with three crowns. Many importers attach great importance to this mark, and erroneously look upon it as a quality mark. A variety of tars differing very much from one another are imported from Sweden. So-called Stockholm tar is generally shipped in three qualities or grades, viz.: fine thin (no grains or crystals), middle fine or ordinary (either gluey or thin and fine-grained), thick (very close-grained). The name 'Umea tar' is applied to similar tar produced in the Umea district and shipped from the port of Umea. This tar is delivered in 'Swedish barrels' containing 27½ galls. and weighing 167 kilos. gross, and 133

kilos. net. 'Umea tar' is considered the best in the market. 'Skelleftea' and 'Lulea' tar are of a similar quality. These three tars are sometimes also shipped as 'Stockholm tar.' Swedish 'factory tar'—obtained from waste wood in charcoal kilns at the saw mills, and produced as a by-product in charcoal burning—must not be confounded with 'Stockholm' or 'Umea' tar. It is easily distinguished by its colour and smell. The genuine tar is yellow-brown or light-brown in colour, and with a turpentine smell, while the factory tar is of a dark-brown or black colour with a strong smoky smell. The tar manufactured by peasants and shipped from Finland (Wasa and Uleaborg) was formerly, and is sometimes now, called 'Stockholm tar,' but is generally shipped as 'Wasa tar.'

Until comparatively recent years there were only two kinds of wood-tar regularly exported to England, viz. Stockholm tar exported from the Gulf of Bothnia, and Archangel tar from Archangel. The latter was shipped in barrels containing about 112 litres. Then the so-called Russian tar exported from Riga, Libau, and Königsberg came on the market, and has largely taken the place of 'Stockholm tar,' owing to the scarcity and high price of the latter, and also because Russian tar is obtainable at all times of the year. Disputes between buyers and sellers as to the real meaning of 'Stockholm tar' have arisen since the appearance of the cheap factory tars on the market, and British importers have suggested that the term 'Stockholm tar' should be retained for the peasant-made article, as it has been used for centuries, and for the 'factory tar' 'Swedish kiln wood-tar.' The Swedish exporters advise that buyers of tar should purchase from samples and insist on a full description of the tar. They much prefer this to a guarantee to sell 'genuine Stockholm tar.' (D. McEwan, Brit. and Col. Drug. 1911, 59, 138; J. Soc. Chem. Ind. 1911, 30, 274.)

STOKESITE. Hydrated silicate of tin (Sn 28 p.c.) and calcium $H_4CaSnSi_3O_{11}$, crystallised in the orthorhombic system. This mineral is known only as a single crystal, about 1 cm. in length, found in an old Cornish collection. It somewhat resembles gypsum in appearance, being colourless and transparent, and with a perfect pearly cleavage. Sp.gr. 3.18, H.=6. It is associated with axinite, and came from Roscommon Cliff, near St. Just, in Cornwall (A. Hutchinson, Min. Mag. 1900, 12, 274.)

Tin occurs as an essential constituent of but few minerals, and of these cassiterite (SnO_2) is the only one of any commercial importance. In Bolivia several sulphide ores of tin have been found, namely canfieldite (v. ARGYRODITE), cylindrite, franckeite, teallite, and stannite (q.v.). The rare nordenskiöldine



and hulsite (q.v.) complete the list of tin minerals. A mineral with the inconspicuous characters of stokesite, occurring probably in granitic and metamorphic rocks, would not attract the attention of prospectors, and quite possibly it is of wider distribution than has hitherto been recognised.

L. J. S.

STOLZITE. Lead tungstate, $PbWO_4$, crystallised in the tetragonal system and

isomorphous with scheelite (CaWO_4) and wulfenite (PbMoO_4). The small pyramidal crystals are grey, greenish, or reddish-yellow in colour; sp.gr. 7.87–8.13; $H.=3$. It is a mineral of sparing occurrence at Zinnwald in Bohemia, Broken Hill in New South Wales, Loudville in Massachusetts, Sardinia, Chile, and Brazil.

A dimorphous form of lead tungstate is the monoclinic mineral *raspite*, of rare occurrence with stolzite at Broken Hill in New South Wales, and also found in gold sands in Brazil.

L. J. S.

STORAX *v.* BALSAMS.

STOVAINE. Trade name for the hydrochloride of dimethylamino-*tert*-amyl benzoate



obtained by acting on dimethylamino-acetone with ethyl magnesium bromide; ethyl dimethylaminopentanol is thus obtained, and on treating with benzoyl chloride gives stovaine. Used as an anæsthetic (*v.* SYNTHETIC DRUGS).

For its detection see Guerbet (Compt. rend. 1920, 171, 40). For its microchemical identification see Denigès (Ann. Chim. anal. 1919, [ii.] 1, 65).

STOWITE *v.* EXPLOSIVES.

STRAMONIUM. *Thorn-apple* (known as Jamestown or Jimson weed in U.S.A.). (*Stramonii folia*, B. P.; *Stramonii semina*. In the United States the leaves only are official. *Stramonium*, U.S. P., which refers to *D. tatula*, L., as well as to *D. stramonium*, L.; *Stramoine*, Fr.; *Stechapfel*, Ger.). The seeds and leaves of *Datura stramonium* (Linn.) are employed in medicine for their sedative and narcotic properties. The former are administered in the form of tincture or solid alcoholic extract, and the latter are smoked as a remedy for asthma. According to De Candolle, the plant is indigenous to the neighbourhood of the Caspian Sea, whence it has spread throughout the temperate and warmer parts of the world (Flück. a. Hanb. 2nd ed. 459; Benth. a. Trim. 192).

Like other drugs derived from the *Solanaceæ*, the physiological action of datura depends upon the presence of poisonous alkaloidal constituents. The dried leaves contain 0.1–0.3 p.c. of alkaloid, the average being 0.22 p.c. (Brit. Pharm. Codex). The U.S. P. demands a minimum of 0.25 p.c. The seeds contain about as much as the leaves (*v.* TROPEINES).

What appeared to be a single alkaloid, 'daturine,' was isolated by Geiger (Annalen, 7, 272). Von Planta (*ibid.* 74, 246, and 252), and subsequently Ladenburg (*ibid.* 206, 279) and Schmidt (*ibid.* 208, 196; Arch. Pharm. [3] 22, 329), have, however, proved that 'daturine' is a mixture of *hyoscyamine*, the alkaloid of henbane, and its isomeride *atropine*, originally obtained from belladonna. In belladonna atropine was supposed to exist together with hyoscyamine, but it has been observed that in the extraction of the alkaloids, the relative proportion of the one to the other depends upon the mode of working. With greater care, the yield of hyoscyamine is increased, and that of atropine diminished, and it is possible to obtain the whole of the alkaloid as hyoscyamine. This fact has been investigated

by W. Will (Ber. 21, 1719), who finds that hyoscyamine may be easily converted into atropine by the action of alcoholic solutions of alkalis or by heat alone. It is probable, therefore, that in belladonna, and also in datura, atropine is not present in the plant, and that it is produced during the process of extraction (*cf.* Schmidt, Ber. 21, 1829; Will and Bredig, *ibid.* 21, 2777). Ladenburg, however, questions this view (*ibid.* 21, 3065).

Scopolamine is also present in the leaves and stalks of *Datura stramonium* (Schutte, Arch. Pharm. 229, 492; Beckurts, Chem. Zentr. 1906, ii. 916).

The seeds yield about one-quarter of their weight of a bland fixed oil, from which Gérard (Compt. rend. 111, 305) has isolated *daturic acid* $\text{C}_{17}\text{H}_{34}\text{O}_2$. It consists of slender needles, which melt at 55° . Two other acids have also been isolated (Holde, Chem. Zentr. 1902, ii. 1417). (For a method of estimation of the alkaloids, see Schmidt, *ibid.* 1900, i. 376; Andrews, Chem. Soc. Trans. 1911, 99, 1871.)

Other species of datura have been investigated by Van den Driessen Mareeuw (*ibid.* 1899, i. 539); Kucher (Arch. Pharm. 243, 309); Schmidt (*ibid.* 244, 66); Pyman and Reynolds (Chem. Soc. Trans. 93, 2077); Andrews (*l.c.*).

F. H. C.

STRASS *v.* GEMS, IMITATION AND COUNTERFEIT.

STRAWBERRY. The fruit of *Fragaria vesca* (Linn.). Many varieties are known.

König gives as the average composition—

	Water	Protein	Invert sugar	Cane sugar	Other N-free sub.	Acidity: malic acid	Fibre	Ash
European	87.0	0.6	5.1	1.1	2.8	1.1	1.6	0.7
American	89.7	1.0	4.8	0.6	0.4	1.4	1.5	0.6

According to American investigations (Bull. 28, U.S. Dept. of Agric. 1899) about three-fourths of the total N present exists as real proteids.

The acidity of strawberries is usually stated to be due to malic acid, but according to Paris (Chem. Zeit. 1902, 26, 248) it is chiefly due to citric acid. On the other hand, Stone (Agr. Science, 1889, 257) states that citric acid can only be present in small quantities, if at all. Stone found that the ratio of acid to sugar is, in wild strawberries 1 : 2, in American varieties 1 : 3.5, and in European varieties 1 : 9.

There appears to be no doubt that American-grown strawberries are richer in protein and acid, but much poorer in total solids, sugar, and cellulose than European ones.

Strawberries contain small quantities of salicylic acid, probably in the form of an ester (Portes and Desmoulières, J. Pharm. Chim. 1901, 14, 342; also Süss, Chem. Zentr. 1903, ii. 841; and Windisch, Zeitsch. Nahr. Genussm. 1903, 6, 447), the amount found being usually about 2 or 3 mgms. per litre of juice. The fatty oil of strawberries has a sp.gr. 0.9345 at $15^\circ/4^\circ$, saponification number 193.7, acid number 6.41, Reichert-Meissl number 2.1, iodine number (Hübl) 180.3. It yields 88.2 p.c. of insoluble fatty acids, their iodine number being 192.3 (Aparin, J. Russ. Phys. Chem. Soc. 1904, 36, 581).

Strawberry root contains a tannin, *fragarin*, of a pale-yellow colour, soluble in water and alcohol, yielding *fragarin* when boiled with dilute hydrochloric acid (Phipson, Chem. News, 37, 135).

The flavour of strawberries is imitated in confectionery by the use of a mixture of 2 parts ethyl acetate and 1 part of amyl acetate.

Strawberries are highly valued as a fruit, and in most cases are easily digested; in the case of a few susceptible persons, however, they produce an urticaria comparable to that produced by eating shell-fish. According to Mendel and Hooker (Amer. J. Physiol. 1902, 7, 380), intravenous injections of an aqueous extract of strawberries produced an increased flow from the thoracic duct, a fall of blood pressure, and a diminution in the coagulability of the blood.

For the effect of manuring upon the yield and especially the earliness of strawberries, v. Dyer and Shrivell (J. Roy. Hort. Soc. 1903, 27, 4), who found that moderate dressings of phosphates and sodium nitrate, applied with a light manuring with dung, slightly increased the yield of fruit, but had a distinct influence upon early ripening; whilst potash salts had an injurious effect, diminishing the yield and retarding maturity. H. I.

STREAM-TIN v. CASSITERITE.

STROMEYERITE. *Argento-cuprous sulphide* or *Argentiferous copper-glance*, AgCuS or $\text{Ag}_2\text{S} \cdot \text{Cu}_2\text{S}$. A mineral crystallising in the orthorhombic system, and isomorphous with copper-glance. Sectile, dark steel-grey colour, shining streak; subconchoidal fracture. H. 2.5–3.0; sp.gr. 6.2–6.3. It was formerly found in some quantity in the Zmeinogorsk mine in the Altai Mountains, Siberia; and is known from several copper mines in North and South America (v. COPPER-GLANCE). L. J. S.

STRONTIANITE. Native strontium carbonate (SrCO_3) crystallising in the orthorhombic system and isomorphous with aragonite and witherite (q.v.). The mineral takes its name from Strontian in Argyllshire, where it was known in the lead mines as early as 1764, and in material from this source the element strontium was discovered. Crystals are rare and usually acicular or spiky in form; more often the mineral is found as columnar or fibrous masses. The colour is usually white or pale-yellowish, but the columnar masses from Strontian show a characteristic and delicate shade of green; sp.gr. 3.7; H. 3½. Strontianite is a mineral known from comparatively few localities, and in quantities sufficient for mining only in the neighbourhood of Münster and Hamm in Westphalia, where it forms veins in calcareous marl of the chalk formation (J. Beykirch, Ueber den Strontianit des Münsterlandes, Jahrb. Min. 1901, 13, 389). A large deposit of strontianite covering an area of 50 acres is reported to have been found at Tidewater, 200 miles north of Vancouver, B.C. It is used for the preparation of strontium hydroxide, which is employed (in preference to the poisonous barium compound) in the refining of beet-sugar. It is also used for producing the red fire of fireworks, and in the manufacture of 'basic bricks.'

Reference. Strontium minerals, Imp. Min. Res. Bur. 1923. L. J. S.

STRONTIUM. Sym. Sr. At.wt. 87.6 (Thorpe and Francis). According to Aston, strontium is simple with an atomic weight of 88 (cf. Aston, Chem. Soc. Abstr. 1924, ii 445).

Strontium derives its name from Strontian in Argyllshire, where strontianite, the carbonate of strontium, was first found. This mineral was suspected by Crawford in 1790 to contain a new earth, the existence of which was confirmed by Hope in 1792, and by Klaproth in 1793.

All primary rocks contain strontium in greater or less quantity. More strontium than barium has been taken up by water, owing to the readier solubility of the sulphate, which is found deposited along with gypsum on evaporation. The carbonate and sulphate of strontium are often found along with deposits of common salt (Dieulafait, Ann. Chim. [v.] 15, 540).

Strontium is chiefly found as the sulphate, *celestine* SrSO_4 , and the carbonate, *strontianite* SrCO_3 . It almost invariably accompanies calcium in traces in the various forms of aragonite and calcite. In *barytocelestine* it occurs along with barium as a mixed sulphate; barytes also generally contain traces of strontium. *Brewsterite* $\text{Al}_2\text{O}_3 \cdot \text{H}_4(\text{BaSr})\text{O}_3 \cdot (\text{SiO}_2)_6 \cdot 3\text{H}_2\text{O}$ is a silicate in which strontium occurs associated with barium. Strontium, in minute traces, is present in the mineral waters of Carlsbad, Kaiser-Franzenbrunnen, and many other places, and in sea-water. According to A. G. Francis (Analyst, 1923, 48, 315–320), brines from bor-holes in Derbyshire, Staffordshire, and Scotland contained the following quantities of barium and strontium, the figures expressing grms. per 1000 grms. of water: Renishaw, depth 3198 ft., Ba 0.93, Sr 0.67; Heath, depth 2870 ft., Ba 1.12, Sr 0.21; Brimington, depth 1350 ft., Ba 0.06, Sr 0.16; Apedale, depth 3570 ft., Sr 0.50; West Calder, depth 3910 ft., Ba 0.58, Sr 0.88. The base exchanging property of zeolites (permutit reaction) may account for the presence of large quantities of barium and strontium chlorides in natural brines (J. Soc. Chem. Ind. 1923, 42, 973 A).

Davy obtained, by a method identical with that described under barium, a metallic body which he supposed to be strontium, but which was probably only a rich amalgam. Matthiessen by the electrolysis of the fused chloride, obtained a metallic-looking mass, and the method was used also by Borchers (Zeitsch. Elektrochem. 8, 759) with similar results. It seems, however, probable that some action similar to that described under BARIUM and CALCIUM occurred, and that a sub-chloride and not the metal was formed, the compound having the property of decomposing water. Strontium may be obtained by Guntz's method as described under BARIUM. The method previously used for the preparation of barium (A. 1913, ii. 504) has been successfully applied to the case of strontium, which is obtained in a pure state by heating silicon (2.5 parts) with strontium oxide (20 parts) in an exhausted iron tube at 1250° for 3 hours (2.1 grms. of strontium were actually obtained). Ferro-silicon, if sufficiently rich in silicon, may be used instead of silicon (C. Matignon, Compt. rend. 1923, 177, 1116; Chem. Soc. Abstr. 1924, 126, ii. 44). An amalgam is obtained by Davy's method, and the greater part of the mercury may be removed by dis-

tillation in a vacuum. The impure strontium so obtained is then treated with hydrogen at a red heat, whereby the hydride is formed and the last traces of mercury removed. The hydride is then decomposed by exhausting the tube and finally raising the temperature to 1100° .

The eutectic point for the binary mixture of strontium chloride and potassium chloride occurs when containing 15 p.c. of the latter salt; this mixture melts at 628° , or 220° lower than the melting-point of strontium chloride. On electrolysing it by the method used for calcium, sticks of strontium 10 cms. long and 1–2 cms. diameter can be obtained. A current density of 25 to 20 amps. per sq. cm. is required and a current efficiency of 80 p.c. is obtained (Electrochem. 1914, 187). B. L. Glascock (J. Amer. Chem. Soc. 32, 1222) used a hemispherical cast-iron vessel of 25 cms. diameter as a container and a carbon anode 8 cms. by 8 cms. With pure strontium chloride as electrolyte, and a current of 125 amperes and 40 volts, 76 grams were obtained in 7 hours. Guntz and Gallio (Compt. rend. 151, 813) obtained crystalline, metallic strontium by heating a mixture of anhydrous strontium oxide with the calculated amount of aluminium powder, for four hours, at 1000° , in a steel tube 10 cms. long and 3 cms. diameter, the iron tube being placed during the operation in an evacuated porcelain tube. On cooling the inner tube is found to be coated with silver-white crystals of strontium, containing 99.4 p.c. of metal; density 2.63. The density of the metal prepared by electrolysis is given by Glascock as 2.55; specific heat 0.0742.

Strontium is a light, malleable metal which has a silvery lustre when freshly cut but rapidly becomes yellow on exposure to the atmosphere and afterwards assumes a white coating of oxide. It reacts with water, methyl and ethyl alcohols, ethyl aceto-acetate, ethyl malonate, and aniline with evolution of hydrogen. It unites with the halogens and phosphorus, and reacts slowly with ethyl iodide, but is without action on silicon tetrachloride. It burns in an atmosphere of carbon dioxide and illuminating gas as energetically as in air, but not so violently as calcium does under similar conditions.

The chief uses of strontium compounds are in sugar refining and pyrotechny, as a substitute for barytes in fillers and in the manufacture of glass and medicines. The world's production of strontium minerals has fallen from 18,425 long tons in 1913 to 4319 tons in 1920, and 7232 tons in 1921. The output in 1921 consisted of 6622 tons of celestine in England, and 610 tons of strontianite in Germany.

Strontium hydride SrH_2 is obtained by heating the amalgam in a current of hydrogen. The mercury distils off, leaving a white solid, which decomposes water, yielding hydrogen and the hydroxide.

Strontium monoxide, or *strontia* SrO , is obtained when the nitrate is heated to redness, or when the carbonate is ignited, either alone or in contact with carbonaceous matter, such as coal or charcoal. Lepaly (Dingl. poly. J. 256, 169), having observed that in the decomposition of strontium carbonate by means of superheated steam the hydroxide so formed loses water at

temperatures near its melting-point, and is converted into a solid mass of oxide, devised a process for the production of strontium oxide upon the large scale. Moist strontium carbonate, moulded into suitable forms, is deprived of a portion of its moisture and heated in retorts placed over a decomposing furnace. Superheated steam is also blown into the retorts, and the liberated carbon dioxide led away. The oxide formed by ignition of the hydroxide is removed in waggons, fresh carbonate being introduced in order to make the process continuous. Specially constructed kilns using generator gas are now usually employed for preparing the oxide by heating the carbonate at a high temperature.

Strontium oxide is a greyish-white porous mass of sp.gr. 3.9, non-volatile, infusible and glowing with a dazzling white light in the oxy-hydrogen flame. It possesses an alkaline taste and reaction. Like lime, when moistened with water, it slakes, becoming hot and falling to powder. If the calculated quantity of water be added to form the crystalline hydroxide, the whole solidifies to a solid mass.

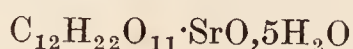
Strontium hydroxide $\text{Sr}(\text{OH})_2$ is the product of the action of water upon the oxide. On dissolving the hydroxide in 5–6 parts of boiling water, filtering hot and allowing to cool in a closed vessel, small transparent quadratic crystals of $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ are deposited; these deliquesce in the air and are rapidly converted into carbonate. Heated to 100° , water is expelled, leaving the hydroxide $\text{Sr}(\text{HO})_2$. This hydroxide may also be obtained in the fused state by heating the crystals to low redness, when they solidify on cooling to a greyish-white crystalline mass. At a red heat all the water is expelled, anhydrous strontia remaining. The crystals of $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ are soluble in 50 parts of cold and 2.4 parts of boiling water, forming strontia-water, which rapidly absorbs carbon dioxide from the atmosphere, becoming coated with a crust of carbonate.

According to Sidersky (Bull. Assoc. Chim. Sucr. 1921, 39, 167), 100 grms. of a solution of the hydroxide in water contain at 0° , 0.90 gm. $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$, at 15° , 1.46 grms., and at 101° (b.p. of solution), 49.75 grms. Sucrose solutions dissolve larger quantities of the hydroxide.

According to Heyer (Ber. 1886, 19, 1684), when strontium hydroxide is heated to bright redness and the oxide so formed exposed to air saturated with aqueous vapour and afterwards to dry air, a crystalline powder of the composition $\text{Sr}(\text{OH})_2 \cdot \text{H}_2\text{O}$ is obtained. Another hydrate $\text{Sr}(\text{HO})_2 \cdot 2\text{H}_2\text{O}$ also exists according to Müller-Erbach (Ber. 1887, 20, 1628).

Strontium hydroxide is used largely in the preparation and refining of beet-root sugar, and in the extraction of crystallisable sugar from molasses. Its use depends upon the property of the oxide and hydroxide of strontium to combine with sugar to form saccharates easily decomposable by carbon dioxide. Lime was formerly used, but strontia is preferable, the precipitated saccharate of strontia being more granular than that of lime. Scheibler stated that to obtain a good yield 3 molecules of $\text{Sr}(\text{OH})_2$ should be employed; if 4 molecules are used 98.4 p.c. of the sugar is precipitated. For 1 kilog. of molasses $\frac{1}{2}$ a kilog. of $\text{Sr}(\text{OH})_2$ in $1\frac{1}{2}$ kilogs. boiling water is a good proportion. The mixture

is stirred, then, after standing nearly a day, the saccharate crystallises out; it is afterwards pressed and washed with cold strontium hydroxide solution. Under increased pressure and temperature a tribasic saccharate is obtained, but if this while hot is introduced into hot water it is decomposed, $\text{Sr}(\text{OH})_2$ crystallising out, and the ordinary saccharate



remaining in solution. On the large scale this clear solution is heated to over 100° when the saccharate is precipitated, impurities remaining in solution. The saccharate is afterwards decomposed by carbon dioxide.

Many processes have been devised for the manufacture of strontium hydroxide, of which the following are the most important:—

In Niewerth's process (Dingl. poly. J. 251, 191), celestine (SrSO_4) is mixed with equal quantities of coal and brown iron ore and roasted. On lixiviation of the product with water, strontium hydroxide and ferrous sulphide are produced.

Claus (Dingl. poly. J. 253, 82) proposes to obtain it from the chloride by addition of an equivalent of barium hydroxide to the hot solution; $\text{Sr}(\text{OH})_2$ crystallises out and barium chloride is recovered by evaporation and crystallisation. Also by adding an equivalent of barium hydroxide to a hot solution of strontium sulphide. It is also found that if a solution of barium sulphide is added to a hot solution of strontium sulphide, strontium hydroxide crystallises out on cooling, barium hydrosulphide remaining in solution. A similar reaction occurs between sodium sulphide and strontium sulphide. On evaporating the solutions of barium or sodium hydrosulphide, mixing with coal-dust, igniting gently and lixiviating, solutions of barium and sodium sulphides are obtained which can be used again. Mother liquors containing strontium hydrosulphide when evaporated and ignited with coal-dust give strontium hydroxide on lixiviation with water. Claus also (J. Pharm. Chim. [v.] 11, 434) describes a process based on the decomposition of strontium monosulphide into hydroxide and hydrosulphide under influence of water, the hydroxide crystallising out.

Lepay's process (Dingl. poly. J. 254, 436) consists in treating strontianite (SrCO_3) with steam superheated to a temperature higher than the melting-point of the hydroxide. The carbonate is introduced into iron pots and is there heated to low redness; the contents are then removed to retorts, into which the superheated steam is blown. The semi-fluid hydroxide flows into a suitable receiver, and is thence run off into moulds. It is best to prepare the carbonate by working it into a paste with 30–40 p.c. weak caustic lye, and converting into balls or hollow cylinders.

Knight (Eng. Pat. 16220, 1884) precipitates strontium sulphide with an equivalent of zinc chloride; after decantation from the precipitated zinc sulphide, the clear solution is decomposed with caustic soda, strontium hydroxide crystallising out on cooling.

Lee Pattinson (Eng. Pat. 16989, 1884) employs the following process: An equivalent of manganese dioxide is added to a solution of strontium sulphide and air of the temperature of

100°F . blown through. About 66 p.c. is converted into hydroxide and 33 p.c. into insoluble thiosulphate, 33 p.c. of the sulphur present being also deposited. The sulphur is extracted by naphtha, and the oxide of manganese used again. If air is blown through only until a precipitate begins to form, two-thirds of the strontium is found to be converted into hydroxide, and on crystallising almost pure hydroxide is obtained. The mother-liquor containing trisulphide is converted into sulphide and used again.

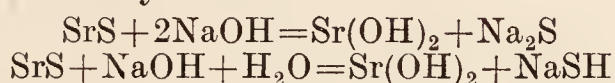
A large quantity of hydrate and strontium carbonate—10,000 to 15,000 tons—was made on the Tyne by the following process. Celestine was decomposed by furnacing with coal in a reverberatory furnace, whereby a 90 p.c. decomposition was effected. The crude SrS was lixiviated and the solution of 20° – 24°Tw . was allowed to cool in shallow pans. One half of the strontium crystallised out as hydrate, which was purified by recrystallisation, and the remaining half was present as strontium hydrosulphide $\text{SrS} \cdot \text{H}_2\text{S}$. The solution was treated with carbon dioxide obtained by the combustion of coke when strontium carbonate was precipitated (mixed with a little free sulphur), hydrogen sulphide being evolved. The carbonate was separated by a filter press and was freed from sulphur by digestion with solution of caustic soda or strontium hydrate. When it was desired to produce the hydrate only and it was commercially practicable, caustic soda was added to the hot concentrated solution of strontium sulphide, whereby the whole of the strontium crystallised out as hydrate, the mother-liquor containing the sodium sulphhydrate. The sources of loss in this process are: (1) imperfect decomposition of the celestine; (2) the ash in the coal (silica, alumina, &c.) fixes and renders insoluble a portion of the strontium; (3) the insoluble residue is of large bulk and is difficult to extract; (4) during lixiviation a portion of the strontia is rendered insoluble by oxidation. But by careful working a yield of 70 p.c. of the available strontia in the celestine may be obtained.

Mactear (Eng. Pat. 5170, 1886) mixes strontium sulphate with slightly more than its equivalent of sodium sulphate and a quantity of carbonaceous matter. The finely-divided mixture is heated in a furnace until the sulphates become reduced to sulphides. The product is treated with hot water, when the two sulphides react, with the production of sodium hydrosulphide and strontium hydroxide, which latter is obtained by crystallisation. The mother-liquor containing the former is evaporated, and the residue used again in reducing a fresh supply of celestine. The strontium hydrosulphide obtained as a by-product in the working of the Claus process may be utilised by mixing it with a solution of sodium sulphide Na_2S , when strontium hydroxide and sodium hydrosulphide are formed, the former of which may be crystallised out as usual.

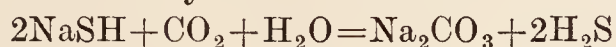
According to Trachsel (J. Soc. Chem. Ind. 1886, 630) other processes for the manufacture of the hydroxide from strontianite and celestine are as follows. If the native carbonate is employed as the raw material, it is first converted into oxide in kilns, the burning requiring a higher temperature than that of lime; the resulting oxide is then dissolved in boiling water, the solu-

tion clarified and crystallised. If the sulphate is used, the process is more complicated. The powdered mineral may be boiled with a solution of sodium carbonate, and the resulting carbonate made into bricks with sawdust and calcined as above. Or a mixture of strontium sulphate and sodium carbonate may be furnaced, also yielding strontium carbonate and sodium sulphate. In a third process ammonium carbonate is used to convert the sulphate into carbonate, the conversion being accomplished in closed vessels provided with stirring apparatus.

Trachsel, in order to simplify the manufacture, has devised the following more direct process. It is based upon the fact that a solution of strontium sulphide treated with caustic soda becomes converted into strontium hydroxide, sodium sulphide or hydrosulphide being simultaneously formed:



The second reaction is more advantageous, requiring only half the soda. The sodium sulphide and hydrosulphide are then converted into carbonate by a stream of carbon dioxide:



The hydrogen sulphide may be utilised by converting it into sulphur dioxide by passing it through a Claus kiln.

The sodium carbonate is next treated with caustic lime, obtaining thereby calcium carbonate and caustic soda, which can be used again, thus rendering the process continuous.

The sulphate fresh from the mine is passed through a crushing apparatus, mixed with 7 cwts. of coal to every 20 cwts. of sulphate, and the mixture calcined in a plus-pressure or revolving furnace, 3–4 hours being sufficient for the conversion into sulphide. It is then carried to the lixiviators, consisting of round or square vats of boiler-plate, each provided at 6 ins. from the bottom with a removable grating of iron bars, on which is spread a filter of sugar bags covered with fragments of brick or other suitable material to protect it from the red-hot furnace charge. In the centre of the grating an upright cast-iron pipe is fixed, passing through the grating but not quite touching the bottom of the vat, and bearing on the top a flat or umbrella-shaped plate, between which and the pipe an interspace is left for the escape of liquor which is forced up by the steam entering through a steam-pipe placed in the centre of the cast-iron pipe at the bottom of the vat, over which it projects several inches. In these vats the charges as they come from the furnace are covered with boiling water or weak liquor from a former operation, and the steam is turned on, which not only keeps the liquor boiling, but also circulates it energetically, forcing the liquor which has percolated through the false bottom upwards in the cast-iron pipe, when it falls back upon the charge. When the liquor has attained the strength of 24°Tw. it is allowed to settle, and then run off to crystallising tanks, where it is treated with a strong solution of caustic soda. The greater part of the strontium hydroxide falls down at once, a further quantity crystallising out on cooling. The mother-liquor (chiefly NaSH) is drained away from the crystals and run into evaporating pans, where it is con-

centrated to 30°Tw. and again run into other crystallising tanks, where it deposits practically all its strontium hydroxide.

The crystals are dried and washed in hydro-extractors and twice re-crystallised, which renders them ready for packing. This double re-crystallisation causes serious loss, but by the following device one re-crystallisation is found sufficient. The impure hydroxide, after being once dried and washed is thrown into a muffle-furnace, where it is gently heated and stirred. Part of the water of crystallisation is thus driven off, the iron sulphide is oxidised, and any strontium sulphide is changed to sulphite, sulphate, and thiosulphate, a little strontium carbonate being also formed. This carbonate is sufficient to precipitate all the iron when the furnace product is dissolved in boiling water. The solution is clarified and allowed to cool, and the crystals, after passing through the hydro-extractor, are ready for packing. By this means also the crystals can be produced in a shorter time, about six days being the average required.

Strontium dioxide SrO_2 is formed as a hydrate when a solution of strontium hydroxide is mixed with one of hydrogen peroxide, shining scales of the composition $\text{SrO}_2 \cdot 8\text{H}_2\text{O}$ being deposited. At a temperature above 50°, and in very concentrated solution, the anhydrous peroxide is obtained. The hydrated peroxide, when heated to 130°, or even in dry air at the ordinary temperature, gives off water, and the peroxide is left in the form of a white powder. On heating this powder to redness, oxygen is evolved without fusion, strontium monoxide remaining. When, however, the monoxide is heated with oxygen (*cf.* Pierce, Brit. Pat. 130840) under a pressure of 105 to 126 kilos. per sq. cm. at a temperature of 400°–500°, the product contains upwards of 85 p.c. of the dioxide and resembles barium dioxide in its physical properties.

Strontium chloride SrCl_2 (m.p. 874°) is formed directly by the combustion of strontium in chlorine, or by heating anhydrous strontia in a stream of chlorine. According to Konigsl-Weisberg (Ber. 12, 511) chlorine has no action on dry $\text{Sr}(\text{OH})_2$, but it converts the hydrate $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ into chloride and chlorate, a small quantity of hypochlorite being also formed. Strontium chloride is generally obtained from strontianite or celestine. The former, dissolved in hot hydrochloric acid, deposits on cooling long hexagonal deliquescent needles of $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ of sp.gr. 1.603, isomorphous with the hydrate of calcium chloride. When heated the crystals lose their water, the white anhydrous salt being left, which fuses at a high temperature, forming a glassy mass of sp.gr. 2.96. According to Mulder, 100 parts of water dissolve 44.2 parts SrCl_2 at 0°, 83.1 parts at 60°, and 101.9 parts at 100°. It is also soluble in alcohol. In the system SrCl_2 — HCl — H_2O , the solid phases occurring at 25° are $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$, and $\text{SrCl}_2 \cdot 2\text{H}_2\text{O}$, and coexist in equilibrium with a solution containing 2.11 p.c. SrCl_2 , and 27.14 p.c. HCl .

The anhydrous chloride absorbs dry ammonia, forming a white powder of the composition $\text{SrCl}_2 \cdot 8\text{NH}_3$. NaCl and SrCl_2 are immiscible in the molten condition; KCl combines with SrCl_2 to form $2\text{KCl} \cdot \text{SrCl}_2$, m.p. 597°, and

$\text{KCl}, 2\text{SrCl}_2$, m.p. 638° (Scholich, Jahrb. Min. 1920 Beil. Bd. 43, 251-294). Strontium chloride forms a double salt with caesium chloride: $5\text{CsCl}_2, 2\text{SrCl}_2, 8\text{H}_2\text{O}$.

Wackenroder (Dingl. poly. J. 253, 440) proposes to prepare strontium chloride on the large scale by adding an equivalent of calcium chloride to strontium sulphide obtained by the reduction of celestine, and passing carbon dioxide into the mixture, when sulphuretted hydrogen is given off and the calcium precipitated as carbonate. The filtered solution is then evaporated to the crystallising-point of the strontium chloride.

Mactear (Eng. Pat. 1915, 1886) mixes celestine and calcium chloride with charcoal or other form of carbon and a little limestone or lime, and strongly heats the mixture in a furnace, the waste fire-gases being utilised to dry the calcium chloride. The product, consisting of strontium chloride and calcium sulphide or oxy-sulphide, yields on lixiviation solutions from which strontium chloride can be crystallised.

Strontium oxychloride. When strontium hydroxide is boiled in a concentrated solution of strontium chloride, the liquid, on cooling, deposits nacreous lamellæ of $\text{SrCl}_2 \cdot \text{SrO} \cdot 9\text{H}_2\text{O}$, easily decomposed by water and alcohol. *In vacuo* this oxychloride loses water, becoming $\text{SrCl}_2 \cdot \text{SrO} \cdot \text{H}_2\text{O}$ (André, Compt. rend. 93, 58). The basic chloride of strontium $\text{SrCl}_2 \cdot \text{SrO} \cdot 9\text{H}_2\text{O}$ exists in solution at a temperature above 20.5° . Below this temperature, $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ and the hydroxide $\text{SrO} \cdot 9\text{H}_2\text{O}$ may coexist as solid phases in contact with aqueous solutions. The solution saturated with respect to these substances at 0° contains 0.31 p.c. SrO and 30.58 p.c. SrCl_2 .

Strontium bromide SrBr_2 is obtained when strontium is burnt in bromine vapour, or when the carbonate is dissolved in hydrobromic acid. From the solution, on evaporating, long needles of the hydrate $\text{SrBr}_2 \cdot 6\text{H}_2\text{O}$ are obtained. It is readily soluble in water and slightly soluble in alcohol. The anhydrous bromide, m.p. 643° , forms a double salt with lithium bromide $\text{LiBr}, 2\text{SrBr}_2$ which decomposes at 503° . With NaBr it forms a simple eutectic at 486° , with KBr the compounds $2\text{KBr}, \text{SrBr}_2$, m.p. 559° , and $\text{KBr}, x2\text{SrBr}_2$, m.p. 574° .

A basic salt $\text{SrBr}_2 \cdot \text{SrO} \cdot 9\text{H}_2\text{O}$ at 25° can only exist in contact with solutions containing from 40.66-49.79 SrBr_2 . The cryohydrate temperature for SrBr_2 is at -28° , and the eutectic solution contains 41.7 p.c. SrBr_2 (Zeitsch. phys. Chem. 92, 59).

Strontium iodide $\text{SrI}_2 \cdot 7\text{H}_2\text{O}$ is prepared by evaporating a solution of hydriodic acid saturated with strontium hydroxide. It crystallises in six-sided plates, very soluble in water. Heated in a closed vessel it may be fused without parting with iodine, but in contact with air iodine fumes are evolved, strontium oxide being left. At 25° SrI_2 yields a basic iodide



which is stable in contact with solutions containing from 49.37-64.04 p.c. SrI_2 .

Strontium fluoride SrF_2 is also similarly obtained by treating the oxide or carbonate with hydrofluoric acid, or by precipitating a soluble strontium salt with sodium fluoride. Strontium

fluoride is a white powder insoluble in water. Its melting-point is 1400° and it crystallises in the cubic system. It forms a double salt with the chloride $\text{SrCl}_2, \text{SrF}_2$, m.p. 962° , D 4.616, which is tetragonal and optically negative.

Strontium carbide SrC_2 has been prepared in the pure crystalline condition by Moissan by reducing the oxide with carbon in the electric furnace, using 120 grms. of strontia to 30 grms. of sugar carbon. The reduction is effected at a lower temperature than the corresponding calcium carbide. It is a brownish crystalline mass, density 3.19, which decomposes water yielding acetylene and strontium hydroxide. Like the corresponding compounds of calcium and barium it absorbs nitrogen when heated in contact with the gas, the most favourable temperature being between 1000° and 1200° —cyanide, cyanamide and a little dicyanamide are produced.

Strontium carbonate SrCO_3 occurs native as strontianite in rhombic crystals, isomorphous with those of aragonite and witherite. Strontium oxide absorbs CO_2 , as does CaO , when strongly heated to a temperature about 1050° , becoming incandescent, the luminosity being greater than that of lime. But the normal carbonate is never formed in this way (Raoult, Compt. rend. 92, 1110). When a solution of a strontium salt is precipitated by an alkaline carbonate, strontium carbonate is obtained as a white powder of sp.gr. 3.62. It may be obtained crystallised in the form of strontianite by fusing a mixture of potassium chloride, sodium chloride and the amorphous carbonate, and allowing to cool (Bourgeois, Bull. Soc. chim. [ii.] 37, 447). When gently heated it becomes converted into strontia. The dissociation of strontium carbonate begins at 1141° , but only becomes rapid at 1255° (Zeitsch. anorg. Chem. 98, 47). A litre of water, according to Fresenius, dissolves 55 milligrams of strontium carbonate. It is still less soluble in aqueous ammonia or ammonium carbonate, but dissolves more readily in ammonium chloride and nitrate. Boiled with ammonium chloride solution it becomes converted into strontium chloride.

Several processes have been devised, in view of the use of strontia in sugar refining, for the production of strontium carbonate on the large scale. Urquhart and Rowell (Dingl. poly. J. 1884, 252) treat native sulphate (celestine) with sulphuric acid to remove iron and aluminium, then boil the product with mixed solutions of sodium sulphate and carbonate. The resulting mixture of strontium sulphate and carbonate is heated in a furnace with excess of Na_2CO_3 , and the mass lixivated, SrCO_3 being thus obtained, together with a liquor which is used for the treatment of fresh celestine.

Mebus and Decastro (Dingl. poly. J. 257, 198) digest finely-pulverised strontium sulphate with a solution of ammonium carbonate, the decomposition being effected in an apparatus fitted with agitating appliances.

A basic hydrated strontium carbonate is formed when the hydrate $\text{Sr(OH)}_2 \cdot \text{H}_2\text{O}$ is exposed to a current of carbon dioxide, and the product dried at 145° (Finkener, Ber. 19, 2958).

Strontium nitride Sr_3N_2 may be obtained by the action of nitrogen on the amalgam at a red heat. The mercury distils off, leaving a dark

fused mass which decomposes water with the formation of ammonia and strontium hydroxide.

Strontium nitrate $\text{Sr}(\text{NO}_3)_2$ may be prepared by dissolving the carbonate in dilute nitric acid. On allowing the hot concentrated solution to evaporate, the anhydrous nitrate separates out in transparent crystals belonging to the regular system, generally in octahedrons modified by faces of the cube. Its sp.gr., according to Schröder, is 2.96. It possesses a cooling taste, and when thrown upon red-hot charcoal deflagrates, burning with a red flame. Owing to the fact that this salt lends itself most readily to the production of red fire, it is much used in pyrotechny.

On cooling a dilute solution of strontium nitrate a hydrate $\text{Sr}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ separates out in large monoclinic prisms, which rapidly effloresce in the air. Strontium nitrate is soluble in about twice its weight of water at 13° , and in an equal weight at 100° (Mulder). It is but slightly soluble in alcohol and almost insoluble in strong nitric acid.

The solubility of the nitrate and hydroxide in presence of each other, at 25° , can be represented by two curves intersecting at a point which gives the composition of the solution, saturated with respect to both substances. This solution contains 1.76 parts of SrO and 81.06 parts $\text{Sr}(\text{NO}_3)_2$ per 100 parts of water.

Strontium phosphide Sr_3P_2 is prepared by reducing tristrontium phosphate with carbon in the electric furnace. It forms brownish-red crystals, density 2.68, and decomposes water yielding phosphoretted hydrogen and strontium hydroxide.

Di-strontium ortho-phosphate $\text{Sr}_2\text{H}_2\text{P}_2\text{O}_8$, or SrHPO_4 , is obtained by precipitation of solutions of strontium salts with disodium phosphate as a white amorphous powder, insoluble in water but soluble in acids or ammonium salts. It is not decomposed by aqueous solutions of alkalis. After being heated strongly to the fusing-point it exhibits phosphorescence.

According to Kühn, a mixture of di-strontium and mono-strontium phosphates is formed when the strontium salt is incompletely precipitated in the cold by the alkaline phosphate.

Potassium strontium phosphate KSrPO_4 , and sodium strontium phosphate NaSrPO_4 , are obtained by ignition of one molecule strontium pyrophosphate with a molecule of potassium or sodium carbonate and extraction with water. They are, however, somewhat readily decomposed by water, the residue being invariably found to contain neutral strontium phosphate. According to Joly (Compt. rend. 104, 905) a molecule of HNa_2PO_4 reacts with one of SrCl_2 in three stages. A gelatinous trimetallic phosphate is first formed, which then becomes crystalline, and is afterwards transformed into di-strontium phosphate, the solution becoming acid. The temperature remains stationary at first, while cubic crystals of $\text{NaSrPO}_4 \cdot 9\text{H}_2\text{O}$ begin to form, almost insoluble in cold water. If the precipitate is allowed to remain in the liquid and phenolphthalein added, and then sodium hydroxide, a white gelatinous precipitate, rapidly crystallising, is formed. When the indicator changes, one equivalent of alkali has been added, and the whole of the strontium is precipitated as $\text{NaSrPO}_4 \cdot 9\text{H}_2\text{O}$.

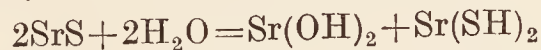
Strontium pyrophosphate $\text{Sr}_2\text{P}_2\text{O}_7$ is obtained by precipitation as an amorphous powder, rapidly becoming crystalline when the liquid is kept warm. It is insoluble in acetic acid but soluble in stronger acids. Heated to 100° the hydrate $\text{Sr}_2\text{P}_2\text{O}_7 \cdot \text{H}_2\text{O}$ is left, but above that temperature the water is driven off.

On adding strontium nitrate to a boiling solution of sodium pyrophosphate, a precipitate forms which is probably a mixture of strontium pyrophosphate with a double salt.

Di-strontium arsenate SrHAsO_4 . When a solution of HNa_2AsO_4 is added to one of SrCl_2 a precipitate of $\text{SrNaAsO}_4 \cdot \text{H}_2\text{O}$ is thrown down; when the filtrate from this is evaporated, a white precipitate of the di-strontium salt is obtained (Salkowski). According to Joly (Compt. rend. 104, 905), when 1 molecule SrCl_2 solution is added to one of HNa_2AsO_4 no precipitate is formed, the solution remaining alkaline; but after some time, if the sides of the vessel are rubbed, a crystalline precipitate separates, and the liquid becomes acid. In 24 hours large cubic crystals of $\text{NaSrAsO}_4 \cdot 9\text{H}_2\text{O}$ (isomorphous with corresponding phosphate) are deposited. On addition of one equivalent NaOH the precipitation is complete.

Strontium silicate. According to Kirwan, equal weights of strontia and silica fuse, with formation of an amber-coloured glass and a black and white enamel. Vauquelin found that with 3 parts of strontia a solid grey mass is formed, difficultly soluble in water, but readily soluble in dilute acids. According to Kuhlmann, strontium carbonate, digested in solution of silica is converted into a hydrated strontium silicate.

Strontium monosulphide SrS is prepared by reduction of the sulphate with coal or other form of carbon. It is a white, granular, semi-fused and brittle mass. It is decomposed by treatment with a large quantity of boiling water, with formation of strontium hydroxide, which crystallises out on cooling, and strontium hydrosulphide, which remains in solution:



If a less quantity of water be employed, nearly pure hydrosulphide is extracted, while the residue on treatment with more water gives a solution of almost pure hydroxide (*cf.* Terres and Brückner, Zeitsch. Elektrochem. 1920, 26, 25).

The strontium sulphide obtained by heating 100 parts SrCO_3 , 30 parts sulphur, and 5 parts arsenious oxide shows a greenish-blue phosphorescence if the carbonate has been prepared from the chloride and ammonium carbonate, but a greenish-yellow if precipitated by sodium carbonate (Verneuil, Compt. rend. 103, 600). According to Becquerel (*ibid.* 104, 551) the colour of the phosphorescence varies with the temperature. At -20° it is violet-blue, at $+40^\circ$ pale blue, at 90° a greenish-yellow, and at 150° orange. The reverse series of colour-changes is noticed as the temperature falls (*cf.* Mourel, Compt. rend. 1915, 160, 174).

Strontium tetrasulphide SrS_4 . When the monosulphide and sulphur are digested in water in the proportion of 1 to 3 molecules, and the solution allowed to evaporate below 17° , a brown syrup is obtained which crystallises at 8° to a mass of the composition $\text{SrS}_4 \cdot 6\text{H}_2\text{O}$. This sub-

stance is very hygroscopic, and soluble in alcohol as well as in water. On exposing the solutions to the air, strontium thiosulphate remains in solution, sulphur and a little SrCO_3 being deposited. On heating the syrup to 100° , or concentrating under the air-pump between 20° and 25° , a light-yellow solid of the composition $\text{SrS}_4 \cdot 2\text{H}_2\text{O}$ separates. Heated above 100° , its own water of crystallisation decomposes it. It is insoluble in carbon disulphide.

When an alcoholic solution of SrS_4 is exposed to air, transparent ruby-red rhombic crystals are formed of the composition $\text{SrO} \cdot \text{SrS}_4 \cdot 12\text{H}_2\text{O}$, which are decomposed by water. They are probably identical with Gay-Lussac's disulphide, which he obtained by allowing a solution of strontium sulphide to stand.

Strontium pentasulphide SrS_5 is obtained when the monosulphide is digested in water with 4 molecules of sulphur, but is only known in solution. On attempting to isolate it by evaporation under the air-pump, a mixture of the tetrasulphide and sulphur is obtained (Schöne, Pogg. Ann. 117, 56).

Strontium hydrosulphide $\text{Sr}(\text{SH})_2$ is readily obtained by saturating strontia water with hydrogen sulphide or by passing the gas through water holding strontium sulphide in suspension. Also by dissolving the monosulphide in a small quantity of boiling water, by which it is decomposed into soluble sulphydrate and insoluble hydroxide. By evaporating the solution obtained by the first method, Berzelius obtained the hydrosulphide in large striated prisms, which on heating melt in their water of crystallisation, then give it off, together with hydrogen sulphide and leave a residue of the monosulphide.

Strontium sulphite SrSO_3 . Strontia commences to absorb sulphur dioxide at 230° with production of SrSO_3 . Strontium sulphite is obtained by double decomposition as a white powder soluble in aqueous sulphurous acid, from which solution the sulphite is again deposited in crystalline grains. The crystals are flat, rectangular tables, which are gradually converted into sulphate on exposure to air.

Strontium sulphate SrSO_4 is found native as celestine in large rhombic crystals and fibrous masses. The name celestine was originally given to the mineral on account of the light-blue tint which it generally possesses. This blue colour is discharged on heating, but the mineral becomes blue again on exposure to radium emanation. By fusing potassium sulphate with excess of strontium chloride Manross obtained well-developed artificial crystals of celestine. Sulphuric acid added to the solution of any strontium salt gives a precipitate of sulphate more or less crystalline. According to Haushofer (J. M. 1887, 1, Ref. 15), solutions containing 0.1 grm. SrCl_2 in 20–80 c.c. water treated with 1 c.c. concentrated hydrochloric acid, give with dilute sulphuric acid very perfect rhombic crystals. Precipitated strontium sulphate has a sp.gr. of 3.7, and fuses on being strongly heated. It is less soluble in hot than in cold water, but is more soluble in acids. According to Fresenius, 1 litre of water dissolves 0.145 grm. at ordinary temperatures and 0.104 grm. at 100° . This aqueous solution at once gives a turbidity with solutions of barium salts. Strontium sulphate dissolves to a con-

siderable extent in a solution of common salt and other saline solutions, but the presence of sulphates or dilute sulphuric acid diminishes the solubility. Unlike barium sulphate, strontium sulphate is completely converted into carbonate by boiling with solutions of alkaline carbonates.

Strontium sulphate is soluble in hot, strong sulphuric acid, crystals of celestine separating out on cooling. If it is heated with strong sulphuric acid to 100° and the solution digested with an excess of salt at a still higher temperature, the acid salt $\text{SrH}_2(\text{SO}_4)_2$ separates as a crystalline powder, which changes on exposure to moist air to the hydrated salt $\text{SrH}_2(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$, forming shining tabular crystals. According to Varenne and Pauleau (Compt. rend. 93, 1016) 1 grm. of SrSO_4 precipitated from the chloride dissolves in 1256 grms. sulphuric acid.

Strontium trithiocarbonate $\text{SrCS}_3 \cdot 4\text{H}_2\text{O}$ is obtained by adding carbon disulphide to a solution of strontium hydrosulphide. On addition of ether, dark red needles of the trithiocarbonate are precipitated which become yellow on drying in a vacuum. It is readily soluble in water (Yeoman, Chem. Soc. Trans. 1921, 119, 49).

Strontium perthiocarbonate is formed by adding carbon disulphide to a solution of strontium disulphide. On addition of ether a red oil separates out which gradually forms yellow crystals, readily soluble in water giving a yellow solution (Yeoman, *l.c.*).

Strontium chromate SrCrO_4 is formed as a lemon-yellow precipitate, composed of slender microscopic needles, when a strong solution of chloride or nitrate of strontium is mixed with one of neutral potassium chromate. After drying over sulphuric acid or at 100° the salt is anhydrous, and remains unaltered on heating. One part of the salt is soluble in 840 parts of water at 16° . It is readily soluble in hydrochloric, nitric, and chromic acids. It dissolves with difficulty in acetic acid, and is insoluble in alcohol. No precipitate is formed in presence of acetic acid if the solution contains for 1 molecule K_2CrO_4 , 1 molecule $\text{Sr}(\text{NO}_3)_2$ or $\text{Sr}(\text{C}_2\text{H}_3\text{O}_2)_2$ and 30 molecules water, or for 1 molecule SrCl_2 , 25 molecules H_2O . The separation from barium by means of K_2CrO_4 is, therefore, not complete, some SrCrO_4 coming down along with the BaCrO_4 (Meschtschersky, J. Russ. Phys. Chem. Soc. 1882, 219).

Bourgeois (J. M. 1880, 1, Ref. 351) prepared SrCrO_4 by heating 2 molecules SrCl_2 with 1 molecule K_2CrO_4 and 1 molecule Na_2CO_3 to bright redness. The SrCrO_4 thus obtained forms beautiful yellow rhombic lamellæ, cleaving parallel to faces of a rhombic prism, and sparingly soluble in water.

Strontium dichromate $\text{SrCr}_2\text{O}_7 \cdot \text{H}_2\text{O}$ was obtained by Preis and Rayman (Ber. 13, 340) by dissolving SrCrO_4 in concentrated chromic acid and drying the product at 100° . It consists of readily-soluble dark-red crystals. A second salt, containing $3\text{H}_2\text{O}$, is obtained in the form of red deliquescent crystals.

Detection and estimation of strontium. Strontium salts colour the flame a characteristic crimson. Examined by the spectroscope, the spectrum is found to consist of a large number of bright lines, of which the orange line

Sr α , the red lines Sr β and Sr γ , and the blue line Sr δ are most characteristic. Even in presence of a large quantity of barium salts this observation affords a ready means of distinguishing strontium.

In its reactions strontium very much resembles barium. It chiefly differs in forming more soluble salts. Thus the sulphate, chromate, and silico-fluoride are considerably more soluble. Hence dilute solutions are only precipitated after some time by sulphuric acid or soluble sulphates, and a solution of strontium sulphate gives an immediate precipitate with soluble barium salts.

The chromate is very much more soluble, a precipitate of stellar aggregates of needles only forming with strong solutions and in absence of much acetic acid. Strontium sulphate is formed after a time if the solution is dilute, but immediately if strong, on addition of a solution of calcium sulphate to one of a soluble strontium salt, and thus strontium may be distinguished from calcium.

Strontium is precipitated from its solutions together with calcium and barium by means of ammonium carbonate. Its separation from associated alkaline earths is generally effected by converting the carbonates to nitrates and extracting the calcium nitrate by ether-alcohol mixture. The barium is then precipitated as chromate.

Strontium may be estimated as carbonate by precipitation with ammonium carbonate and ammonia from a hot solution; the carbonate is not decomposed by heating over an ordinary Bunsen burner. It may also be estimated as sulphate, the completion of the precipitation being effected by addition of alcohol. This method, of course, can only be used when the original strontium salt is soluble in alcohol.

Atomic weight of strontium. Richards, using the bromide, obtained as mean 87.616; O=16. Thorpe and Francis (Proc. Roy. Soc. 83 A. 277), using various methods, obtained as mean 87.649.

G. S. B.

STROPHANTHIN v. STROPHANTHUS.

STROPHANTHUS. *Strophanthi semina*, B. P.; *Strophanthus*, U.S. P. *Kombé* and other arrow-poisons. The seeds of various species of *Strophanthus* are used by the natives of Central Africa for the preparation of arrow-poison. A paste is made by crushing the seed with water, and with this the arrow-heads are smeared. Arrows thus tipped appear to be used both in warfare and in the chase. In the latter case the animal falls quickly, when the flesh immediately around the wound is cut away and the remainder eaten without any injurious effect. *Strophanthus* arrow-poison is very widely used throughout the whole of Central Africa, specimens having been obtained and sent to Europe from time to time from nearly all parts of the east and west coasts. The plants are woody climbers of the natural order *Apocynaceæ*, which ascend the highest trees and hang in festoons from one to another. The pods contain one to two hundred seeds, each seed weighing about half a grain, and having attached to it a beautiful comose appendage on an extremely brittle stalk. The seed was first examined by T. R. Fraser, of Edinburgh, in 1872, who drew attention to its important physiological action

on the movements of the heart, and pointed out that both its physiological and toxic action depends upon the presence of an active constituent to which he gave the name 'strophanthin' (Pharm. J. [iii.] 3, 523; 19, 660).

See for an account of the history of the introduction of *Strophanthus*, particularly of *S. Kombé*, Holmes, Pharm. J. 1923, [iv.] 57, 347.

The seeds of several species of *Strophanthus* occur in commerce and have been examined from time to time; as they differ chemically and as sometimes the seeds of different species are mixed, the uncertainty of the botanical identification has rendered much of the earlier chemical work doubtful. It seems best to follow the plan introduced by Thoms and widely adopted in Germany, of designating the various glucosides by the initial letter of the specific name of the plant from which they are derived; thus *k*-strophanthin is the glucoside from *S. kombe*, *g*-strophanthin from *S. gratus*, &c. We will consider the principal species separately; for a description of the botanical characters of their seeds, see British Pharmaceutical Codex, pp. 1003-1004; Holmes, Pharm. J. [iii.] 21, 233; Brit. Pharm. Additions, 1890, 29; Holmes, Pharm. J. [iii.] 16, 778; 17, 903; Maisch, *ibid.* [iii.] 17, 972; Hanausek, *ibid.* [iii.] 17, 972; Perrédès, *ibid.* April 27, 1901; Blondel, J. Pharm. chim. [v.] 17, 249, 297, 554; Christy, Pharm. J. [iii.] 20, 318.

Strophanthus kombe (Oliver) is the only species which is official in the British Pharmacopœia, but the U.S. P. admits in addition *S. hispidus*. *S. kombe* was formerly considered to be a mere variety of *S. hispidus*, and was the first species to be examined, by Fraser. Transverse sections of the seeds moistened with 80 p.c. sulphuric acid, show a green coloration, as do the seeds of *S. hispidus*; various other species give a red colour. The coloration and the physiological action is in each case due to the strophanthin. The seeds of *S. kombe* contain about 30 p.c. of fat, 4 p.c. of ash, a small amount of choline, trigonelline and saponin and 2-3 p.c. *strophanthin*, a physiologically active glucoside which is official in the United States (*strophanthinum*, U.S. P.). According to Heffter and Sachs (Biochem. Zeitsch. 1912, 40, 83) and Brauns and Closson (Arch. Pharm. 1914, 252, 294), there is a crystalline *k*-strophanthin and an amorphous variety; the latter authors distinguish a second amorphous variety formed by the action of water on the crystalline glucoside. *Strophanthin* is prepared by freeing the powdered seeds from fat by means of light petroleum and then extracting them twice with 70 p.c. alcohol. The first alcoholic extract, after concentration to a syrup, may deposit crystals of *k*-strophanthin on keeping. It is better, however, to evaporate the alcohol, precipitate impurities by basic lead acetate (Arnaud, Compt. rend. 1888, 107, 179), remove the excess of lead from the filtrate by hydrogen sulphide, and evaporate still further at 40°-45°, small quantities of alcohol being occasionally added until the end of the operation, when all the alcohol is removed by distillation. The crystalline *k*-strophanthin which separates on keeping may be recrystallised by solution in alcohol at 40°-45°, concentration of the solution,

addition of water and removal of the alcohol by evaporation. It cannot be recrystallised from alcoholic solution and is readily converted into an amorphous variety by water (Brauns and Closson). Heffter and Sachs evaporated the filtrate from lead sulphide in the presence of calcium carbonate, to ensure a neutral reaction, and obtained a yield of crystals equal to 0.4–0.5 p.c. of the seeds, more than by the original Arnaud process. Other processes yield larger quantities of an amorphous product, and are apparently the only ones used commercially. Fraser used a tannin method, similar to Homolle's method for preparing digitalin (*q.v.*). Thoms (Ber. 1898, 31, 271) begins according to Arnaud's method, but removes the excess of lead quantitatively with ammonium sulphate, and after filtration, precipitates the strophanthin by a further large addition of the same salt. It is then dissolved in alcohol and precipitated by ether.

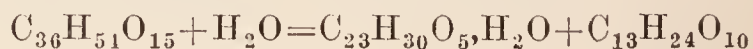
Crystalline k-strophanthin ($C_{40}H_{56}O_{15} \cdot 3H_2O$, according to Brauns and Closson, but see below), forms colourless microscopic needles and plates and melts at about 165° , when hydrated and at 178° – 179° (177° – 181°) when anhydrous; in aqueous solution $[\alpha]_D = +28.7^\circ$ (Heffter and Sachs, Brauns and Closson); soluble in 50 parts of water at 18° . According to Brauns and Closson it is transformed by water to an amorphous acidic substance $C_{40}H_{58}O_{16}$, melting at 165° – 170° if hydrated or at 180° if anhydrous and having $[\alpha]_D = +20.6^\circ$. This would seem to be identical with strophanthin hydrate of Arnaud and to be the hydroxy-acid, of which the crystalline strophanthin is the lactone (*see below, Strophanthidin*); it is not clear whether it occurs as such in the seeds. These contain, however, an *amorphous strophanthin* for which Heffter and Sachs give $[\alpha]_D = +11.87^\circ$; it sinters at 170° and is much more soluble in water than the crystalline variety. According to Heffter and Sachs it is identical with the strophanthin studied chemically by Feist (Ber. 1898, 31, 534; 1900, 33, 2075; *cf.* Jacobs and Heidelberger, J. Biol. Chem. 1922, 54, 253, who give to anhydrous strophanthidin the formula $C_{23}H_{32}O_6$); they found the formula $C_{40}H_{66}O_{19}$ and $[\alpha]_D = +10.12^\circ$, but appear to have taken no special pains to purify the amorphous commercial specimen. However, all the substances mentioned above, and also *h-strophanthin* (from *S. hispidus*) yield on hydrolysis the same crystalline *strophanthidin*, and as Feist also identified the sugar portion, the formula of his strophanthin is best calculated from that of its fission products (Windaus and Hermanns, *see below*). Brauns and Closson have not definitely identified the sugar portion of crystalline *k-strophanthin* which does not seem to contain arabinose, thereby differing from Feist's (amorphous) strophanthin.

The following two colour reactions are given by strophanthidin and by the above strophanthins: With sulphuric acid (preferably 80 p.c.) a bright green coloration changing at 43° – 49° to dark brown, violet, violet-blue, and finally violet-black. A few drops of concentrated sulphuric acid added, with shaking, to 2 c.c. of a solution of strophanthin in acetic anhydride, gives a transitory red colour, changing with or

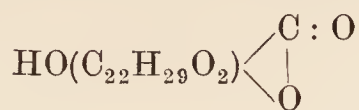
without gentle warming to a pure green (Liebermann's cholesterol reaction). Further, a trace of strophanthin dissolved in a drop of water and mixed with ferric chloride and a drop of sulphuric acid, gives a reddish-brown precipitate which either at once or after a few hours changes to emerald green (Helbing, J. Soc. Chem. Ind. 1891, 575). Strophanthin when warmed with hydrochloric acid and resorcinol gives a rose coloration whilst ouabain gives no coloration, a difference due to the action of the respective sugars formed in the hydrolysis. For colour reactions of strophanthin *see also* Reichard, Pharm. Zentr. Halle, 1915, 56, 159, 174. The hydrolysis of (amorphous) *k-strophanthin* was carried out by Feist by warming gradually on the water-bath a solution in 5 parts of 0.5 p.c. hydrochloric acid; at 75° strophanthidin begins to crystallise out. The other fission product is *strophanthobiose methylether* $C_{13}H_{24}O_{10}$, which sugar forms a crystalline powder, melting at 207° ; by further hydrolysis it is split into one molecule of methyl alcohol, one of *d*-mannose, and one of *d*-rhamnose (Feist, *l.c.*). It is the source of the methoxyl found in amorphous *k-strophanthin* by Zeisel's method; strophanthidin does not contain a methoxy-group. According to Brauns and Closson crystalline *k-strophanthin* does not yield a pentose or rhamnose on hydrolysis, although it gives the same strophanthidin.

Strophanthidin ($C_{27}H_{38}O_7$ or more likely $C_{23}H_{30}O_5$) differs from the parent substance in being almost insoluble in water; it is readily soluble in alcohol, acetone and glacial acetic acid, almost insoluble in ether and petrol. It crystallises from 5 parts of methyl alcohol + 10 parts of water in hard, nacreous plates, m.p., about 171° . It is very bitter; besides giving the above colour reactions it couples with diazonium salts and reduces ammoniacal silver solution slightly. $[\alpha]_D$ in methyl alcohol = $+44.0^\circ$ (Windaus and Hermanns) + 44.26° (Brauns and Closson) + 41.0° to $+41.5^\circ$ (Heffter and Sachs). The yield of strophanthidin from amorphous *k-strophanthin* is mostly given as about 46 p.c. (Feist 50–52 p.c.); from crystalline *k-strophanthin* 56–58 p.c. (Heffter and Sachs).

Windaus and Hermanns (Ber. 1915, 48, 979, 991) have made the interesting discovery that strophanthidin is identical with cymarigenin, a hydrolytic product of the glucoside cymarin from *Apocynum cannabinum* of the same N.O. as *Strophanthus* and having similar physiological properties. Numerous concordant analyses of the substance from both glucosides and of a number of its derivatives led them to adopt the formula $C_{23}H_{30}O_5 \cdot 1\frac{1}{2}H_2O$ for the air dry substance. The water of crystallisation is lost completely only in a vacuum at 115° . In spite of the analytical difficulties owing to this tenacious retention of water, the above formula seems thoroughly established and should doubtless be substituted for $C_{27}H_{38}O_7$ adopted by Feist and by Brauns and Closson. The formula for amorphous *k-strophanthin* of Feist, $C_{40}H_{66}O_{19}$, which is still more difficult to determine by analysis, would become $C_{36}H_{54}O_{15}$ and the equation for the hydrolysis



Strophanthidin is a hydroxy-lactone and is hydrolysed by alkalis to a crystalline acid, m.p. 168°, so that the formula may be resolved into



Jacobs (Bio-Chem. J. 1923, 57, 553, 569) considers that strophanthidin is $\text{C}_{23}\text{H}_{30}\text{O}_5$; crystalline *k*-strophanthin is $\text{C}_{32}\text{H}_{48}\text{O}_{12}$ or $\text{C}_{31}\text{H}_{46}\text{O}_{11}$, and the sugar $\text{C}_9\text{H}_{18}\text{O}_7$ or $\text{C}_8\text{H}_{16}\text{O}_6$.

Straub (Biochem. Zeitsch. 1916, 75, 132) has determined the following subcutaneous lethal doses per gram of frog (*Rana temporaria*):

(Amorphous?) *k*-strophanthin 0.00075 mg.; strophanthidin 0.0025 mg.; benzoyl strophanthidin 0.025 mg. For comparison the corresponding doses of allied substances may be given: digitoxin 0.0036 mg.; digitoxigenin 0.006 mg.; cymaric acid 0.0008 mg.; cymaric acid 0.42 mg. According to Brauns and Closson the activities of crystalline *k*-strophanthin and of amorphous acidic substance derived from it are in the ratio 3 : 1.

The estimation of strophanthin in seeds and tinctures is based on shaking out the strophanthidin, formed by hydrolysis, with chloroform (Lampart and Müller, Arch. Pharm. 1913, 251, 609). The physiological assay is, however, preferable (see U.S. P.).

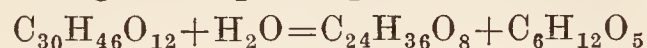
Strophanthus oil has been examined by Matthes and Rath (Arch. Pharm. 1914, 252, 683), f.p. 16°–17°, D_{15}^{20} 0.9252, n_D^{40} 1.4615, $\alpha \pm 0^\circ$, acid number 17.61, saponification number 189.99, ester number 172.38, iodine number (Hübl) 94.97, Reichert-Meissl number 1.31, Polenske number 0.59, Hehner number 93.90, yields a positive elaidin reaction; 21 p.c. of saturated fatty acids (30 p.c. stearic and 70 p.c. palmitic), 73 p.c. of unsaturated fatty acids (20 p.c. of linolic and 80 p.c. of oleic), 7.97 p.c. of glycerol. It contains only one phytosterol, namely sitosterol (see also Heiduschka and Wallenreuter, Arch. Pharm. 1914, 252, 704).

h-Strophanthin, from *S. hispidus* was obtained in a yield of 2.3 p.c. of the seeds by Heffter and Sachs (l.c.). It is amorphous; $[\alpha]_D = +13.9^\circ$; sinters and melts 160°–190°. It gave a yield of 38–39 p.c. of strophanthidin, identical with that from *k*-strophanthin. These observations relate to seeds which were identified botanically with certainty. Most of the older observations on *S. hispidus* refer either to what is now called *S. kombe* (e.g. those of Fraser) or refer to species of doubtful identity (e.g. Kohn and Kulisch, Ber. 1898, 31, 514). Thoms (Ber. 1898, 31, 271) and Karsten (Ber. Deut. pharm. Ges. 1902, 12, 241) seem, however, to have worked with fairly pure *hispidus* seeds. *S. sarmentosus* seeds were examined by Fraser and Mackenzie (Trans. Roy. Soc. Edin. 1910, 47, ii. 341); they contain a glucoside having a pharmacological action similar to that of *S. hispidus*, and are probably used as an arrow-poison in Nigeria. The dried extract is coloured brown and then violet by sulphuric acid.

From the seeds of *S. glaber* of Gaboon, Catillon (J. Pharm. Chim. 1888, [v.] 17, 334) prepared a crystalline strophanthin which is coloured reddish-brown by concentrated sulphuric acid, differing thereby from *k*-strophan-

thin and *h*-strophanthin. Catillon's substance was probably identical with ouabain, the active principle of the wood of *Acocanthera ouabaio* (N.O. Apocynaceæ), which is used by the Somalis as an arrow poison. Ouabain was studied in some detail by Arnaud (Compt. rend. 1888, 106, 1011); the same substance was later found by him more abundantly in the seeds of *Strophanthus glaber* of Gaboon (Compt. rend. 1888, 107, 1162; 1898, 126, 346, 1208). Thoms (Apoth. Zeit. 1900, 15, 753; Ber. Deut. pharm. Ges. 1904, 14, 104) found it also in seeds used for making a Cameroon arrow poison and Gilg identified these seeds as *S. gratus* = *S. glaber* (Ber. Deut. pharm. Ges. 1902, 12, 182). The same substance has been described by Fraser and Tillie (Pharm. J. 1895 [iv.] 1, 76) as *acocantherin* from the wood of *Acocanthera Schimperii*.

Ouabain, better known in Germany as *g*-strophanthin, is a well defined, highly potent substance; it can be prepared fairly easily crystalline, according to Arnaud's method (lead acetate; crystallisation by spontaneous evaporation of solution in 85° p.c. alcohol), from the seeds of *S. gratus* which contain about 3.6 p.c. It forms quadratic plates, soluble at 50° in 100 parts of water and in 30 parts of absolute alcohol. It has the composition $\text{C}_{30}\text{H}_{46}\text{O}_{12} \cdot 9\text{H}_2\text{O}$; the water of crystallisation is lost at 105°, and the anhydrous substance melts at 187°–188°; laevorotatory. If concentrated sulphuric acid is poured under a 1 p.c. aqueous solution, the upper layer becomes pink or red, the lower dirty green; sulphuric acid colours the solution red. Apart from these colour reactions it differs also from *k*- and *h*-strophanthin in not furnishing a crystalline strophanthidin on hydrolysis with acids. According to Arnaud it is hydrolysed by heating with 2 p.c. sulphuric acid thus:



into rhamnose and a product which loses water forming a resin $\text{C}_{24}\text{H}_{28}\text{O}_4$.

For pharmacological action of ouabain see Gley (Compt. rend. 1888, 107, 348); for clinical application (of *g*-strophanthin), Schedel (Ber. Deut. pharm. Ges. 1904, 14, 120).

The United States Pharmacopœia utilises ouabain as a pure crystalline standard for the biological assay of digitalis, strophanthus, and squill. V. DIGITALIS (assay).

Identification of Strophanthin.—Ouabain so closely resembles strophanthin that the identification of the latter is not so easy as at first sight might appear. Strophanthin dissolves in 40–43 parts of water at 15°, while ouabain requires 150 parts. They differ in optical rotation, but the quantity required for the determination is prohibitive. An aqueous solution of strophanthin froths when shaken, while that of ouabain does not. More satisfactory is the following colour reaction which is given by strophanthin but not by ouabain:—To 4 or 5 c.c. of strong hydrochloric acid in a test-tube add a few crystals of resorcin and then a few crystals of the glucoside under examination. Strophanthin gives slowly in the cold, more quickly when warmed in a water-bath, a pink coloration; with ouabain the solution remains colourless. The reaction succeeds with less than a milligram of substance, but it is better to take two or three

milligrams.—A. Richaud (J. Pharm. Chim. [7] 24, 161).

A saponin from *S. gratus* has been described by Sieburg (Ber. Deut. pharm. Ges. 1913, 23, 278) under the name *g-strophanthic acid*, together with its colour reactions. G. B.

STROPHANTOBIOSE *v.* CARBOHYDRATES.

STRÜVERITE. A black mineral closely allied to rutile (TiO_2) and hitherto referred to that species, but containing variable amounts of tantalum, columbium, and iron, as illustrated in the following analyses: I, Strüverite from tin-bearing alluvium on the Sebantun River, Perak (also SiO_2 0.20, H_2O 0.50, MnO trace). II, Strüverite from the Etta tin mine, Black Hills, South Dakota (also SiO_2 2.0, H_2O 0.4). III, Strüverite from Craveggia, Piedmont (also CaO 0.51, MgO 0.17, MnO trace). IV, Strüverite from Ampangabe, Madagascar (also Al_2O_3 1.80). V, Ilmenorutile from the Ilmen Mountains, Urals (also CaO trace). VI, Ilmenorutile from Iveland, Sætersdal, Norway (also CaO 0.11, MgO trace).

	I.	II.	III.	IV.	V.	VI.
TiO_2	45.74	47.8	41.20	71.15	53.04	54.57
SnO_2	2.67	1.3	—	0.05	—	—
Ta_2O_5	35.96	34.8	23.48	10.14	14.70	—
Cb_2O_5	6.90	6.2	23.48	—	21.73	32.15
FeO	8.27	7.3	11.38	15.84	10.56	12.29
Total	100.24	99.8	100.22	98.98	100.03	99.12
Sp.gr.	5.30	5.25	5.59	4.91	5.14	4.64

The composition has been explained by the presence of the molecules $\text{Fe}(\text{TaO}_3)_2$, $\text{Fe}(\text{CbO}_3)_2$, and FeTiO_3 in solid solution in the rutile, or as isomorphous mixtures with titanyl titanate $(\text{TiO})\text{TiO}_3$. The name *strüverite* is restricted to those members of the series richer in tantalum, and the name *ilmenorutile* is applied to those richer in columbium. The tetragonal crystals have angles very close to those of rutile, tapiolite (FeTa_2O_6), &c. They often exhibit a curious distortion, due to elongation in the direction of a pyramid-edge, which together with twinning gives rise to a pseudo-orthorhombic habit. The material is iron-black and opaque with a brilliant lustre on the fresh fracture; $H.=6$. It is infusible before the blowpipe; dissolves by digestion for several days in hot concentrated sulphuric acid, and is decomposed by heating in chlorine. These minerals occur in pegmatite-veins, at times in some abundance, and crystals up to 6 kgs. have been found in Madagascar. In addition to the localities mentioned above, ilmenorutile is known also from Western Australia. L. J. S.

STRUVITE. Hydrated ammonium magnesium phosphate $\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$, crystallised in the orthorhombic system with hemimorphic development, and identical with the well-known crystalline precipitate obtained by mixing ammoniacal solutions of sodium phosphate and a magnesium salt. In nature it was first observed after the great fire of Hamburg in 1842, when large numbers of beautiful, colourless to yellowish crystals, up to an inch across, were found in peaty earth intermixed with cattle-dung amongst the foundations of the St. Nicholas church. Found in such a situation, these crystals with their curious coffin-like shape attracted much attention. This form and also the pyroelectric character of the crystals depend on their hemimorphism. Sp.gr. 1.71; $H.=2$. On exposure

to air the crystals become dull, opaque, and white, due to loss of ammonia and water. For this reason, specimens should be preserved in sealed vessels. Since the discovery at Hamburg, struvite has been recognised to be of common occurrence, but always in connection with organic remains. It is found in cesspools, sewers, dung-heaps, &c.; and under more natural conditions in guano deposits—both in bird-guano on islands and in the bat-guano of caves—and in a mammoth's tusk found in a swamp in Yukon. It has also been observed in urinary calculi, tartar of teeth, and is formed by the putrefaction of urine. Good crystals may be obtained artificially by mixing two solutions, one containing 20 grms. of $(\text{NH}_4)_2\text{HPO}_4$, 10 grms. of $(\text{NH}_4)_2\text{SO}_4$, and 12 grms. of phosphoric acid (sp.gr. 1.555) in 80 c.c., and the other 16 grms. $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ in 120 c.c. When allowed to remain in contact with the liquid the crystals of struvite become altered into newberyite ($\text{HMgPO}_4 \cdot 3\text{H}_2\text{O}$). Since struvite is of ready formation and is practically insoluble in water, the addition of Epsom-salt to farmyard manure would assist in the retention of ammonia and phosphates. L. J. S.

STRUXINE. An alkaloid found by Schaefer (J. Amer. Pharm. Assn. 1914, 1677) in a shipment of partly decomposed *nux vomica* bean from Cochin China, or strychnine isolated by Boorsma (Bull. Inst. Bot. de Buitz, 14, 3) from the leaves of *S. nux vomica* (Pharm. J. 1924, 113, 97).

STRYCHNINE *v.* NUX VOMICA. Cf. Oliveri Mendala and Comella, Gazz. chim. ital. 1923, 53, i. 276.

Strychnine nitrate not infrequently contains brucine. The following modifications of Keller's method is used by Gordin for the quantitative separation of strychnine and brucine: A quantity of 0.2 gm. of the alkaloid is dissolved in 15 c.c. of 3 p.c. sulphuric acid, and when cold, treated with 3 c.c. of a cold mixture of equal parts of nitric acid (1.42) and water. Brucine is decomposed, with the formation of oxidation products, which are not soluble in chloroform after making alkaline with sodium hydroxide solution. Therefore the mixture is shaken in a separating funnel in the presence of excess of sodium hydroxide solution with successive quantities of chloroform (20 c.c., 10 c.c., and 10 c.c.). The chloroform extracts are evaporated, and the residue of strychnine dried at 110°C . until the weight is constant. A freshly-prepared mixture of 0.1002 gm. of strychnine nitrate and 0.1021 gm. of brucine nitrate gave, on analysis, 0.1004 gm. of strychnine nitrate (Reck, Chem. Zeit. 1924, 48, 166; Analyst, 1924, 49, 237).

For the estimation of *nux vomica* preparations, see Deane and Edmonton (Pharm. J. 1924, 113, 96).

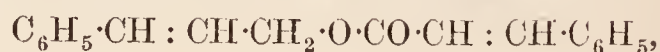
For the assay of *strychnos cinnamomifolia*, and a note on the determination of strychnine, see Short (Pharm. J. 1924, 113, 97).

STYPHNIC ACID *v.* PHENOL AND ITS HOMOLOGUES.

STYPTICINE *v.* OPIUM.

STYPTOL. Trade name for cotarnine phthalate.

STYRACIN, *cinnamyl cinnamate*



occurs in storax. It crystallises in needles, m.p. 14° . On saponification it forms a salt of cinnamic acid and styrene (*v.* BALSAMS).

STYRACOL *v.* SYNTHETIC DRUGS.

STYRENE, *styrolene*, *cinnamene*, *phenylethylene* $C_6H_5 \cdot CH : CH_2$, occurs in liquid storax (*v.* BALSAMS), from which it may be obtained on distillation. It is formed by reducing phenylacetylene with zinc-dust and acetic acid (Aronstein and Hollemann, Ber. 1889, 22, 1184); by heating cinnamic acid with barium hydroxide (Gerhardt and Cahours, Annalen, 1841, 38, 96); by acting upon cinnamyl alcohol with sodium amalgam (Hatton and Hodgkinson, Chem. Soc. Trans. 1881, 39, 319); by heating dragon-blood resin either alone or in the presence of zinc-dust (Bötsch, Monatsh. 1880, 1, 610); by heating phenylethyl bromide with alcoholic potash (Thorpe, Zeitsch. Chem. 1871, 130); by the action of aluminium chloride on a mixture of benzene and ethyl bromide (Anschütz, Annalen, 1886, 235, 331); by acting upon phenylmethylcarbinol with phosphoric acid (Klages and Allendorff, Ber. 1898, 31, 1298). Styrene is, however, most conveniently prepared by acting upon cinnamic acid with hydriodic acid and then heating the product with aqueous potash (Fittig and Binder, Annalen, 1879, 195, 137), also by brominating ethylbenzene to $\alpha\beta$ -dibromoethylbenzene and treating this with metallic magnesium (Braun and Moldänke, Ber. 1921, 54, [B.] 618).

Properties and reactions.—Colourless aromatic liquid; sp.gr. 0.925 at 0° ; b.p. 146° ; insoluble in water, but soluble in all proportions in alcohol and ether. On keeping it changes gradually into metastyrene, but the change is never complete, indicating that the final stage is one of equilibrium; benzene solutions of styrene and metastyrene undergo no change in the dark, but on exposure to sunlight the refractive index of the styrene solution gradually rises, whilst that of the metastyrene solution gradually falls. With the halogens and halogen acids it readily forms addition compounds; on reduction it yields phenylethane and on oxidation benzoic acid; by the action of nitrogen trioxide it is converted into a nitrite (Sommer, Ber. 1895, 28, 1328).

Sodium in liquid ammonia forms ethylbenzene and sodamide (Lebeau and Picon, Compt. rend. 1913, 157, 223; condensation with formaldehyde yields β -phenyltrimethylene glycol, b.p. $176^{\circ}/13$ mm. (Prins, Proc. K. Akad. Wetensch. Amsterdam 1919, 22, 51).

Distyrene $(C_8H_8)_2$, m.p. 124° , is obtained by the distillation of calcium cinnamate (Engler and Leist, Annalen, 1833, 6, 256) or cinnamic acid alone (Miller, *ibid.* 1877, 189, 340), and also by the distillation of truxillic acid (Liebermann, Ber. 1889, 22, 2255). A liquid distyrene is said also to exist, being obtained when styrene is heated with concentrated hydrochloric acid (Erdmann, Annalen, 1883, 216, 187).

Metastyrene. Styrene on keeping, especially at high temperatures, changes, slowly in the dark, more quickly under the influence of light, into another polymer, which forms an amorphous glassy mass, metastyrene; on distillation it regenerates styrene.

α -Chlorostyrene $C_6H_5 \cdot CCl : CH_2$ is obtained by heating styrene chloride with soda-lime

(Blyth and Hofmann, Annalen, 1845, 53, 310); liquid b.p. 199° .

ω -Chlorostyrene $C_6H_5 \cdot CH : CHCl$ is formed when cinnamic acid is heated with sodium hypochlorite or with potassium chlorate and hydrochloric acid (Stenhouse, Annalen, 1845, 55, 1; 1846, 57, 79); also by heating phenylchlorolactic acid with water to 200° (Glaser, *ibid.* 1870, 154, 166); also by the action of zinc-dust on trichloromethylphenylcarbinol (Jocitsch, Chem. Zentr. 1899, i. 607).

$\omega\omega$ -Dichlorostyrene $C_6H_5 \cdot CH : CCl_2$ is formed by the action of chloral on benzene in the presence of aluminium chloride (Biltz, Annalen, 1897, 296, 259).

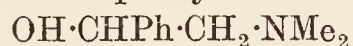
$\alpha\omega$ -Dichlorostyrene $C_6H_5 \cdot CCl : CHCl$ is formed by the action of phosphorus pentachloride on acetophenone (Dyckerhoff, Ber. 1877, 10, 120).

$\alpha\omega\omega$ -Trichlorostyrene $C_6H_5 \cdot CCl : CCl_2$ is obtained by the action of alcoholic potash on phenyltetrachlorethylene (Biltz, Annalen, 1897, 296, 270).

Bromostyrenes are obtained by similar methods (Glaser, *ibid.* 1870, 154, 168; Fittig, *ibid.* 1879, 195, 142; Fincke, *ibid.* 1883, 216, 290; Jocitsch, Chem. Zentr. 1899, [i.] 607; Favorsky, *ibid.* 1899, [i.] 778; Nef, Annalen, 1899, 308, 273; Dufraisse, Compt. rend. 1920, 171, 960).

***p*-Bromodichlorostyrene**, $C_6H_4Br \cdot CH : CCl_2$, m.p. 23° – 24° , b.p. 138° – $140^{\circ}/15$ mm. (Jocitsch, J. Russ. Phys. Chem. Soc. 1902, 34, 971).

Styrene forms two isomeric *iodohydrins*, $OH \cdot CHPh \cdot CH_2I$ and $CHPhI \cdot CH_2 \cdot OH$. Both react with dimethylamine to give the same ω -dimethylamino- α -phenylethanol



which is also obtained by the action of dimethylamine on styrene (Tiffeneau and Fourneau, Bull. Soc. chim. 1913, [iv.] 13, 971 *idem*, 1914, [iv.] 15, 275).

Iodostyrenes (*v.* Peratoni, Gazz. chim. ital. 22, [ii.] 69; Liebermann and Sachse, Ber. 1891, 24, 4155).

ω -Nitrodihydroxystyrene



yellow needles, m.p. 155° (decomp.) (Rosenmind).

***o*-Nitrostyrene** (m.p. 12°) from β *o*-nitrophenylpropionic acid and alkalis (Einhorn, Ber. 1883, 16, 2213).

***m*-Nitrostyrene** (m.p. -5°) is similarly obtained (Prausnitz, *ibid.* 1884, 17, 597).

***p*-Nitrostyrene** (m.p. 29°) similarly obtained (Basler, Ber. 1883, 16, 3005).

ω -Nitrostyrene (m.p. 58°) from styrene and nitric acid (Simon, Annalen, 1839, 31, 269); by heating benzaldehyde with nitromethane and zinc chloride (Pribs, *ibid.* 1884, 225, 321); by heating phenylisocrotonic acid with fuming nitric acid (Erdmann, Ber. 1891, 24, 2773).

For other *nitrostyrenes*, see Pribs, Annalen, 1888, 245, 343; Friedländer and Mahly, *ibid.* 1885, 229, 224; Friedländer and Lazarus, *ibid.* 1885, 229, 233; Lipp, Ber. 1884, 17, 1070.

ω -Chloro-*p*- ω -dinitrostyrene



yellow needles, m.p. 150° – 153° (Pfeiffer, Ber. 1914, 47, 1755).

ω -Bromo-*m*-nitrostyrene, needles, m.p.

76°–77° (Reich and Kochler, Ber. 1913, 46, 3727).

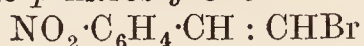
$\omega\omega$ -Dibromo-*m*-nitrostyrene, m.p. 58°.

cis- $\alpha\beta$ -Dibromo-*m*-nitrostyrene, m.p. 50°–51°.

$\alpha\omega\omega$ -Tribromo-*m*-nitrostyrene, m.p. 90°

(Reich and collaborators, Arch. Sci. phys. nat. 1918, 54, 191).

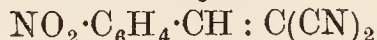
ω -Bromo-*p*-nitrostyrene



pale yellow needles, m.p. 45°–46°. Its stereoisomeride melts at 123°.

ω -Bromo-*o*-nitrostyrene $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{CHBr}$ is similarly obtained in two forms, yellow, m.p. 70°, and a yellow oil; each furnish a tribromo-compound, m.p. 80° (Reich and Chang, Helv. Chim. Acta, 1920, 3, 235).

$\alpha\omega$ -Dicyano-*o*-nitrostyrene



colourless needles, m.p. 137·5°–138° (Heller and Wunderlich, *ibid.* 1914, 47, 1617).

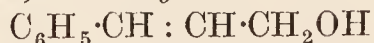
STYROGALLOL (*o*-Dihydroxyanthracoumarin) $\text{C}_{16}\text{H}_8\text{O}_5$ is prepared by heating 10 parts of cinnamic acid with 17 of gallic acid and 150 of sulphuric acid for 2–3 hours at 45°–55°. The yellowish-red mass, after cooling, is poured into a large excess of water, the pale green microscopic crystals so formed are filtered off and washed with boiling, slightly acidified water, and recrystallised from alcohol, glacial acetic acid, or aniline (D. R. P. 40375; Frdl. 1877–87, 569; Jacobson and Julius, Ber. 1887, 20, 2588; Kostanecki, *ibid.* 3137).

Styrogallol forms light yellow needles which do not melt at 350° and sublime at 360° almost without decomposition. It is sparingly soluble in alcohol, acetic acid or aniline, and almost insoluble in other solvents. It dissolves in alkalis with a green colour, which on warming becomes blue, violet, and finally red. It dissolves in strong sulphuric acid with a yellowish-red colour, and when oxidised with nitric acid it yields much phthalic acid.

Styrogallol is a dyestuff which gives on mordanted materials similar shades to nitro-alizarin.

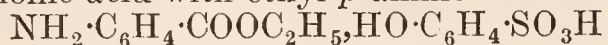
With acetic anhydride it yields a *di*- and a *tri*-acetyl derivative, and when the former is digested with boiling alcohol and potassium acetate for about 2 hours, it yields a crystalline purple-coloured *potassium salt* $\text{C}_{16}\text{H}_7\text{O}_5\text{K}$ (Perkin and Wilson, Chem. Soc. Trans. 1903, 139), which readily dissolves in water with a red colour. With fuming sulphuric acid styrogallol forms a *sulphonate*. When *p*-coumaric acid is condensed with gallic acid it forms *hydroxy-styrogallol* or 2 : 3 : 6-trihydroxyanthracoumarin $\text{C}_{16}\text{H}_8\text{O}_6$, which resembles styrogallol, but the presence of an additional hydroxy group causes it to be less soluble and more intensely coloured. *Triacetoxystyrogallol* $\text{C}_{16}\text{H}_5\text{O}_2(\text{OAc})_3$ melts at 250° in a vacuum (Slama, Chem. Zentr. 1899, ii. 967).

STYRONE, *cinnamyl alcohol*



occurs in storax. It crystallises in thin needles; m.p. 33°; b.p. 250°; it has a characteristic smell of hyacinths. On mild oxidation it yields cinnamaldehyde; with more vigorous oxidising agents it gives cinnamic acid.

SUBCUTIN. A combination of *p*-phenol sulphonic acid with ethyl *p*-amino-benzoate



Used as a local anæsthetic (*v.* SYNTHETIC DRUGS).

SUBERIC ACID (Ger. *Korksäure*)



Obtained by the oxidation of the following substances with nitric acid: cork (Markownikow, Ber. 1893, 3089; Étaix, Ann. Chim. [vii.] 9, 384); castor oil (Markownikow, Étaix, *l.c.*), for details, *see* Day, Kon and Stevenson, Chem. Soc. Trans. 1920, 117, 641; Tilley, Annalen, 39, 166); oleic acid (Laurent, *ibid.* 28, 258; Bromeis, *ibid.* 35, 96); stearic acid (Bromeis, *ibid.* 35, 89); linseed oil (Sacc, *ibid.* 51, 226); cocoa-nut oil (Wirz, *ibid.* 104, 271); almond oil, spermaceti (Arppe, *ibid.* 120, 292; 124, 89); palmitic acid (Schröder, *ibid.* 143, 33); paraffin (Pouchet, J. 1874, 358); by treating pyrrolidine with cyanogen bromide and phosphorus pentachloride (Braun, Chem. Zentr. 1908, ii. 1993); by treating the copper derivative of dipropargyl with iodine, followed by carbon dioxide and reducing the $\Delta^{\beta\epsilon}$ -hexadine- $\alpha\zeta$ -dicarboxylic acid thus formed with hydrogen and platinum black (Lespieau and Vavon, Compt. rend. 148, 1322; 149, 997); by the oxidation of azelaone with potassium permanganate (Derlon, Ber. 1898, 1962). It has been synthesised from trimethylene bromide, magnesium and carbon dioxide (Zelinsky and Gutt, *ibid.* 1907, 3049), and by the electrolysis of an aqueous solution of the potassium salt of the monoethyl ester of glutaric acid and subsequent hydrolysis of the diethyl ester thus formed (Brown and Walker, Annalen, 261, 119). To separate suberic acid from azelaic acid, which is also produced in many of the above reactions, use is made of the different solubilities of their magnesium salts (Gantter and Hell, Ber. 1881, 1552; Derlon, *ibid.* 31, 1959; *cf.* Day, Kon and Stevenson, *l.c.*).

It crystallises in white scales, m.p. 139·5° (Massol, Bull. Soc. chim. [iii.] 17, 746); sparingly soluble in water and ether, insoluble in chloroform. By heating suberic acid with chalk, suberone (*cycloheptanone*), carbon dioxide, water and a trace of benzene are formed (Markownikow, Ber. 1893, Ref. 813; *cf.* Aschan, Ber. 1192, 45, 1603; Day, Kon and Stevenson, *l.c.*). The *anhydride*, obtained by heating suberic acid with acetyl chloride, melts at 62°–63° (Anderlini, Gazz. chim. ital. 24, i. 474). The *amide* melts at 208°. Twenty-six isomerides of suberic acid have been prepared.

SUBERONE *v.* KETONES.

SUBLAMIN *v.* SYNTHETIC DRUGS.

SUBLIMATION. The passage of a stable substance, when heated, into the state of vapour may take place in one of three ways:—

1. The substance is liquid under ordinary conditions; it boils at a definite temperature, depending on the pressure.

2. The substance is solid; when heated it melts at a definite temperature, and when more strongly heated it boils like an ordinary liquid.

3. The substance is solid; when heated it does not melt, but passes directly from the solid state to that of vapour at a definite temperature depending on the pressure.

Similarly in the condensation of vapour we may have (1) liquefaction; (2) liquefaction and

subsequent solidification; (3) direct passage from the gaseous to the solid state.

The term *distillation* is applied to vaporisation and subsequent condensation of the first kind, *sublimation* to the corresponding changes of the third order.

Vaporisation and condensation of the second kind should be included under the term *distillation*, since it is really liquid which is converted into vapour, and which, as a rule, is first formed in the process of condensation. The term sublimation is, however, not unfrequently employed in the case of substances whose melting-points are high or are not far removed from their

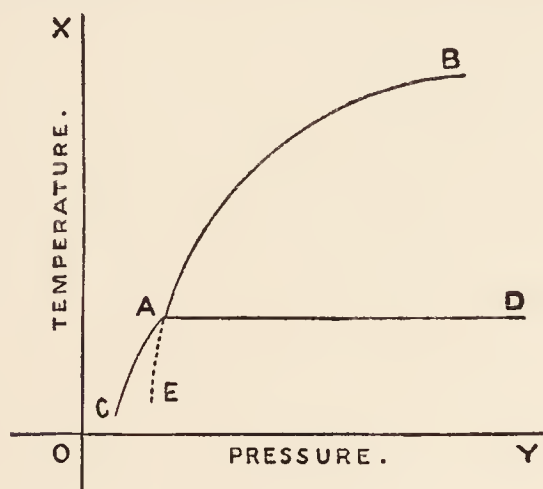


FIG. 1.

boiling-points, and, indeed, if the application of the term were strictly limited to changes of the third class it would not be very frequently employed in practical chemistry.

As a matter of fact, the majority of substances may undergo either distillation or sublimation, according to the pressure under which the vaporisation and condensation take place. This may be best understood by means of the diagram (Fig. 1), in which temperatures are measured as ordinates and pressures as abscissæ.

The curve AB represents the boiling-points of a substance, the curve CA its subliming-points, and the curve AD its melting-points under varying pressures. The boiling- and subliming-points

vary greatly with alteration of pressure, the melting-points to so slight an extent that the curve AD, drawn to true scale for any substance, could not be distinguished in such a diagram from a straight horizontal line.

All three curves intersect each other at A, called the *triple point*. The temperature at A, measured vertically from the horizontal axis OY, gives the melting-point of the substance under the pressure represented by the horizontal distance of A from the vertical axis OX; it is practically the same as the melting-point under atmospheric pressure—generally a small fraction of a degree lower.

If a solid substance is heated under pressures greater than the *triple-point pressure*, its temperature will rise until the melting-point is reached; then, after fusion, the temperature will again rise until the liquid reaches its boiling-point. The melting- and boiling-points under any given pressure are indicated by the intersection of a vertical line representing that pressure with the curves AD and AB.

If, however, the pressure is lower than the triple-point pressure, the substance cannot, under ordinary circumstances, exist in the liquid state at all, and when heated it sublimes without previous fusion at a temperature given by the intersection of the vertical line of constant pressure with the curve CA. (It is, however, possible to cool a liquid below its freezing-point without solidification taking place, and it may, indeed, be made to boil below its freezing-point. This is indicated by the dotted line AE, which is simply a continuation of the curve BA.)

The pressure at the triple point varies very greatly for different substances, but in the vast majority of cases it is far below atmospheric pressure. Hence under ordinary conditions true sublimation rarely takes place.

The following table gives the melting-points, the boiling-points under normal pressure, and the triple-point pressures of a few substances; complete data have been obtained in only a limited number of cases:—

Substance	Melting-point—degs.	Boiling-point—degs.	Triple-point pressure
Water	0·0	100·0	4·6 mm.
Acetic acid	16·4	118·5	9·45 „
Benzene	5·6	80·2	35·9 „
Bromine	—7·1	58·7	44·5 „
Nitrogen	—214	—193·1	60·0 „
Iodine	114·3	184·3	91·0 „
Camphor	180·0	204·0	380·0 „
Mercuric chloride	288·0	303·0	554·0 „
Carbon hexachloride	188 (about)	188 (about)	1 atm.
Arsenious oxide	200 (about)	?	a little above 1 atm.
Aluminium chloride	180–185	?	a little above 1 atm.
Arsenic	500 (about)	450 (about)	above 1 atm.
Carbon dioxide	—57 (about)	—78·2	about 5·3 atm.

Some other compounds—such as mercurous chloride and indium trichloride—sublime without fusion, but exact data are wanting.

It will be seen from the table that the triple-point pressure of carbon dioxide is over five atmospheres, hence when the liquid is allowed to escape from a steel cylinder in which it has been stored under pressure, that which escapes

vaporisation at once solidifies and cannot be melted in an open vessel, but passes directly into the gaseous state.

Arsenic and arsenious oxide also sublime when heated under atmospheric pressure, and carbon hexachloride sublimates if the pressure is very slightly lowered, but melts and distils if the pressure is slightly raised. Water again

cannot exist as a stable liquid under a pressure lower than 4·6 mm. Below this pressure, ice, when heated, sublimcs without melting.

Metals are capable of being sublimed at low pressures. Iridium (in nitrogen at 20 mm. pressure), copper (in nitrogen at 1 mm.), iron and tungsten (in a high vacuum) are sensibly volatile at temperatures considerably below the melting-points. In addition to volatilisation as ordinarily understood there is evidence of straight-line emission of particles of metal. The data for a number of metals, for which information is available, are collected in the table below; the volatilisation was detected mostly at low pressures. Kaye and Ewen (Proc. Roy. Soc. 1913, A, 89, 58).

A formula for the calculation of sublimation pressures has been proposed by Van Ziempt, and has been applied to a number of metals: tungsten, platinum, molybdenum, copper, tin, lead, zinc, silver, bismuth, cadmium, antimony, and gold (Zeitsch. anorg. Chem. 1920, 111, 280; 114, 105).

The curve CA (Fig. 1) represents not only the subliming-points of a solid substance under varying pressures, but also the vapour pressures of the substance at varying temperatures (Ramsay and Young, Trans. Roy. Soc. 1884, i. 37), just as the curve AB represents both the boiling-points and the vapour pressures of the substance in the liquid state; hence the relation of the subliming-point of a solid to the pressure may be defined in precisely the same way as that of the boiling-point of a liquid.

The ordinary definition of the 'boiling-point' (a liquid boils when its vapour pressure is equal to the superincumbent atmospheric pressure) is, however, to some extent misleading. There is, in the first place, perhaps some ambiguity about the terms 'boiling-point' and a 'boiling' liquid. It is true that when a liquid is described as boiling, the impression conveyed is that the liquid is in a state of ebullition, but the 'boiling-point' is certainly not the temperature of ebullition. What is called the 'boiling-point' of a liquid is usually determined by placing a thermometer in the vapour over the liquid, care being taken that the thermometer

vapour may form below the liquid, not only has the pressure of vapour or air over the liquid to be overcome, but also that of the column of liquid over the point where the bubble forms, and, lastly, the adhesion of the liquid to the solid surface (or possibly the cohesion of the liquid itself). In the case of a very clean smooth vessel, and a liquid free from dissolved air, this last factor becomes very important, and the ebullition-point may be considerably higher than the 'boiling-point.' Under the most favourable conditions it is somewhat higher (Regnault, 'Relation des Expériences,' 1847, 525-529).

The boiling-point of a liquid is, in fact, not its ebullition-point—which does not depend solely on the pressure—but it is the *highest temperature attainable by the liquid under a given pressure of its own vapour when evaporating with a perfectly free surface, and when heat is received from outwards towards the surface.* It is only under these conditions, where ebullition is obviously impossible, that the boiling-point can be accurately determined by measuring the temperature of the liquid itself (Ramsay and Young, Chem. Soc. Trans. 47, 42).

In the case of sublimation this difficulty does not occur, for anything analogous to ebullition is impossible, and since the solid can only be in partial contact with the vessel containing it there is practically always a free surface for evaporation.

The ordinary definition of the 'boiling-point' of a liquid takes no account of the fact that a law analogous to Dalton's law of partial pressures holds good for distillation and sublimation.

That this is the case is proved by the behaviour of two non-miscible liquids when distilled together (*v.* DISTILLATION). It is found that the boiling-point and the composition of the mixed vapour are independent of the relative quantities of the two liquids present, and that the 'boiling-point' is the same as that of either liquid when distilled alone under a pressure equal to its partial pressure in the mixed vapour. Hence, as the pressure of the vapour of the one liquid is without influence on the 'boiling-point' of the other, it might be inferred that the pressure of an indifferent gas, such as the air, would be without influence on the 'boiling-point' of a liquid or on the subliming-point of a solid. This is, in fact, the case, and it is really not the pressure of the atmospheric air, but that of the vapour itself in contact with the liquid or solid, that influences the 'boiling-' or subliming-point.

In ordinary cases of distillation or sublimation the vapour of the substance completely expels the air from the flask or retort; hence the substance is surrounded by its own vapour at the same pressure as that of the external atmosphere and the 'boiling-' or subliming-point does depend—though indirectly—on the atmospheric pressure.

But if the substance be made to vaporise in the open air, or in such a manner that the rapid diffusion of the vapour prevents the complete expulsion of the air from the immediate neighbourhood of the substance, then the 'boiling-' or subliming-point does not depend on the atmospheric pressure.

Thus water, when distilled in the ordinary way under a pressure of 15 mm., boils at about 18°, but Schrötter observed in 1853 (Annalen, 88,

—	Boiling-point		Volatilisation detectable at	M.p. at 1 atmos.
	At 1 atmos.	In vacuo		
Mercury .	357°	160°	—39°	—39°
Potassium .	760	370	63	63
Sodium .	880	420	97	97
Cadmium .	778	450	160	321
Zinc .	918	550	180	419
Bismuth .	1420	1000	269	269
Lead .	1525	1150	360	327
Silver .	1955	1400 ?	680	961
Copper .	2310	1600 ?	400	1084
Tin .	2270	1700 ?	360	232
Gold .	2530 ?	1800 ?	1370	1064
Iron .	2450	—	950	1500
Platinum .	2500 ?	—	1200	1750

bulb is always moistened by condensed liquid. It is, in fact, the condensing-point of the vapour that is directly measured.

On the other hand, in order that a bubble of

188) that when some water was placed on a shallow clock glass, supported by a short tripod on a second clock glass, in a bell-jar over sulphuric acid, the temperature fell to -3° when the pressure was reduced to 15 mm. More rapid diffusion and removal of vapour was effected by suspending in the bell-jar a thermometer the bulb of which was covered with a sponge soaked in water; in this case, under a pressure of 40 mm., at which the 'boiling-point' of water under ordinary conditions is 34° , the temperature fell to -10° .

The following experiments afford a still more striking proof of the correctness of the statement that the 'boiling-point' does not necessarily depend on the atmospheric pressure. A copper air-bath was heated to 205° and a thermometer, the bulb of which was covered with cotton wool and moistened with boiling water, was suspended in the bath through an opening at the top. The pressure of the atmosphere was 748 mm., and the water on the cotton wool was in a strongly-heated chamber, yet the temperature, instead of remaining at nearly 100° , fell to 66° , and remained constant at this point while the water rapidly evaporated. A second experiment was carried out under the same conditions, except that steam was introduced, so as to replace the air as completely as possible by aqueous vapour. The temperature of the bath was in this case 195° , and the steam was passed into it after the temperature of the water on the thermometer bulb had fallen to 69° ; the result was an immediate rise of temperature, the highest point reached being 89° . A fall of temperature to 80° was again observed on allowing some of the steam to escape.

In these cases the 'boiling-point' certainly does not depend on the pressure of the surrounding atmosphere, and in all probability the observation that the temperature of a drop of water in the spheroidal state does not reach 100° (under normal atmospheric pressure) may be explained in the same way, the vapour round the drop of water being always diluted with a certain amount of air. Again, by passing a current of air through water or any other liquid boiling in an ordinary distillation bulb, the vapour above the liquid becomes diluted, and the result is an immediate fall in temperature, both of the liquid and of the vapour, although the liquid continues to distil rapidly, and this is the case even when heated air is introduced.

Thus by bringing about admixture of air with the vapour surrounding a vaporising substance the same effect is produced as by reducing the pressure in an ordinary distillation bulb, and in this way, in certain cases, the partial pressure of the vapour may be reduced below the triple-point pressure, so that the substance which in a bulb or test-tube would melt first and then boil, will under these circumstances sublime at a temperature below the melting-point. If the bulb of a thermometer, by repeated immersion in melted camphor, be completely covered by the solid substance, and if the thermometer be then suspended in a strongly-heated air-bath through which a moderate current of air is passing, the camphor will not melt, but will sublime at a temperature lower than its melting-point, although the total pressure is far above the triple-point pressure of camphor.

The slow volatilisation of camphor, iodine,

snow, and other substances is to be explained in precisely the same way, vaporisation always taking place when the partial pressure of the vapour in the surrounding air is less than the vapour pressure of the solid substance.

Again, if the vapour of a substance which is solid at the ordinary temperature condense in the narrow neck of a retort or distillation bulb, the liquid state is first as a rule assumed, and solidification afterwards takes place; but if the same vapour be allowed to diffuse into the air, or if by any means sufficient air be mixed with it before condensation occurs, it frequently happens that the solid state is at once assumed without intermediate passage through the liquid state. This direct passage from the gaseous to the solid state must, in fact, occur if by admixture with any indifferent gas the partial pressure of the heated vapour falls below the triple-point pressure before the temperature falls sufficiently for condensation to take place.

Thus on boiling sulphur in an ordinary retort, while the vapour is rising and before the air has been expelled, the formation of small quantities of flowers of sulphur is always to be observed above the vapour; but when the air has been expelled and the sulphur vapour condenses in the neck of the retort, liquid is formed. When, however, as in the formation of flowers of sulphur on the large scale, the heated vapour is passed into a large chamber containing air, direct condensation to the solid state occurs until the temperature of the chamber reaches the point at which the partial pressure of the sulphur vapour is higher than the triple-point pressure, when liquefaction takes place.

The phenomenon is still more readily observed in the case of camphor, iodine, and other substances, the triple-point pressures of which are relatively high. Thus if we heat one of these substances in a porcelain basin and hold a cold glass funnel or a glass plate over it, the substance melts and boils in the basin, but condenses as a solid on the funnel or plate. The heavy vapour collects in the basin, so that its partial pressure in the atmosphere surrounding the substance soon rises above the triple-point pressure, when fusion takes place; but before reaching the cold glass surface the hot vapour becomes so diluted with air that the partial pressure falls below the triple-point pressure, so that when condensation takes place the solid state is at once assumed. A convenient apparatus for the sublimation of iodine in the laboratory is described by Koehler (*Chem. Zeit.* 1915, 39, 122). In the purification of crude anthracene by passing steam, heated to about 230° , over the melted substance, and condensing the vapour in a chamber by jets of cold water, the steam acts as an indifferent gas, and in all probability the partial pressure of the anthracene vapour is far below the triple-point pressure when condensation takes place.

So also when condensation of moisture from the atmosphere occurs at a temperature below 0° , and when the partial pressure of the aqueous vapour is necessarily lower than 4.6 mm., there must be direct passage from the gaseous to the solid state, and the light crystalline snow flakes present all the appearance of having been formed in this way.

Although the process of sublimation is in

theory quite analogous to that of distillation, yet the apparatus employed for distillation is unsuited for sublimation, for the narrow condensing tubes would rapidly become blocked by the solid sublimate. In cases of true sublimation, therefore, and also in the distillation of liquids with high solidifying points—such as anthracene, camphor, iodine, &c.—the condensing tube must be wide and comparatively short, as in the Silesian subliming pots for arsenic trioxide (*v.* ARSENIC) and in the condensers employed for the manufacture of iodine (*v.* IODINE).

Special arrangements to prevent the blocking of the tubes through which the vapours pass from the sublimation chamber have been patented by F. Bayer & Co. (D. R. PP. 332196, 334669, and 343319, 1919). The tubes extend longitudinally downwards through the sublimation chambers and are enlarged where they leave the chambers. Solid matter is prevented from falling into the tubes by means of plates fixed above the upper open ends. Loss of heat is

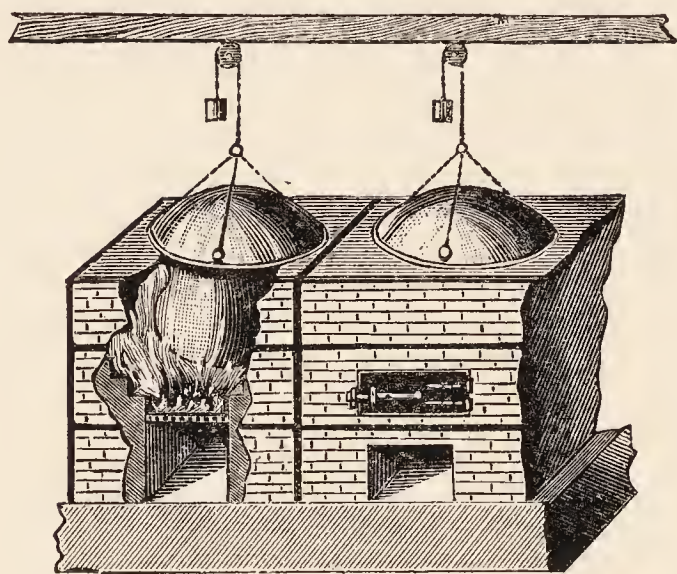


FIG. 2.

avoided by making the tubes outside the chambers double-walled with non-conducting material between the walls. The vapour is led downwards on to a rotating drum, the solid deposited on the drum being removed by scrapers and falling into receptacles which may be changed from time to time to effect fractionation.

The condensing tube may, indeed, be replaced by a simple flat or concave cover over the subliming pot, as in the case of ammonium chloride (Fig. 2).

The ammonium chloride is heated in the pots, and condenses in the solid state on the iron covers.

(It is true that in this case the process, under ordinary conditions, is not one of simple sublimation, since the vapour does not consist of ammonium chloride, but of a mixture of ammonia and hydrogen chloride; there is really dissociation and recombination instead of vaporisation and condensation, but practically the process is the same as that of sublimation.) It has been observed, however, by H. B. Baker (Chem. Soc. Trans. 65, 615; 73, 422) that ammonia will not combine with hydrogen chloride when both gases are very carefully dried, and that dry ammonium chloride does not undergo dissociation when converted into vapour. Johnson (Zeitsch. physikal. Chem. 61, 457) has made the remarkable observation that

the vapour pressures of ammonium chloride are practically the same whether the solid is carefully dried and therefore stable or imperfectly dried and subject to dissociation.

A suitable plant for the sublimation of naphthalene on the large scale is described in Young's 'Distillation Principles and Processes,' Macmillan, 1922; *v.* also Brit. Pat. 179991, 1921. Plants for large scale sublimation have been patented by Sartakoff (U.S. Pat. 1284787, 1918) and Kluchansky (*ibid.* 1304572, 1919).

Various patents have been taken out for the sublimation and fractional condensation of naphthalene and other solid substances. In one plant (D. R. P. 315958, 1918) the vapour is led into an inner chamber, passing then into one or more outer chambers surrounding the inner one, and finally into a cooling chamber. The purest product is condensed in the inner chamber and a crude oil in the cooling chamber. A somewhat similar arrangement is described in the Eng. Pat. 173789, 1920. Another method is to pass the vapour, with or without a current of heated air or inert gas, through a series of chambers kept at graded temperatures (Eng. Pat. 142902, 1919; U.S. Pat. 1324716-7, 1919). Each chamber may contain perforated screens and a cooled baffle extending across it (Eng. Pats. 173723 and 174013, 1920).

It frequently happens that when direct condensation to the solid state takes place, the substance assumes the form of a fine light crystalline powder, or of feathery flakes which are easily carried about by currents of air; hence longer flues or a succession of condensing chambers is required to prevent loss of substance. This is especially the case with such poisonous substances as arsenic or arsenic trioxide, and the condensing tubes attached to the Silesian subliming pots already referred to are supplemented by condensing chambers.

If the sublimation does not take place from a retort or pot, but from a furnace through which the hot gases pass as well as the vapour of the subliming substance, the light sublimate is very liable to be carried away, and the flues must be very long or the chambers very numerous (*v.* ARSENIC).

For a convenient apparatus for vacuum sublimation by an electric heater, specially adapted for the sublimation of large quantities of organic substances, see Moréy (J. Amer. Chem. Soc. 1912, 34, 550); and for an electrically heated sublimation pan, see Jap. Pat. 30605, 1917.

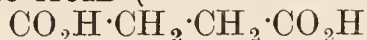
An apparatus for quantitative sublimation has been described by A. V. Fuller (Chem. Analyst, 1920, 29, 6; and Chem. Abstracts, Amer. Chem. Soc., 1920, 14, 3607).

J. Joly (Phil. Mag. 1913, 25, 301) has devised an instrument, the apophorometer, by means of which very small quantities of a solid may be sublimed and the sublimate collected and examined microscopically or chemically. The substance, finely powdered, is placed on a ribbon of thin platinum through which a current can be passed so as to raise its temperature to any required degree. Watch glasses are fixed above and below the ribbon so as to enclose the substance, and the whole may be placed in a receiver which may be exhausted or filled with an indifferent gas. The sublimate collects on the watch glasses.

A process of micro-sublimation has been employed in recent years for the examination of drugs, etc., and a general review of the work on this subject is given by Dezanì (Giorn. farm. Chim. 64, 394; Chem. Zentr. 1916, I, 1044).

S. Y.

SUCCINIC ACID (*Bernsteinsäure*)



Occurs in amber, associated with succoxy-abietic and succino-abietolic acids, succinin, and a yellow powder, succinoresin (*v.* RESINS), in fossil wood and lignite (Reich, J. 1847-48, 499); in unripe grapes (Brunner and Brandenburg, Ber. 1876, 982); in various plants; in ripe wheat and barley grains (Vaudin, Ann. Agron. 1897, 23, 232); in the wood of *Goupia tomentosa* (Aubl.) (Dunstan and Henry, Chem. Soc. Trans. 1898, 228); in the juice of the sugar cane and in the calcium precipitate formed during the treatment of beet juice (Lippmann, Ber. 1891, 3299); in *Orites excelsa* (R.Br.) and other proteaceous trees as aluminium succinate (Smith, Chem. News, 88, 135); in the castor oil plant (Gram, Chem. Zentr. 1903, ii. 450); in the urine of oxen, horses, goats, and rabbits; in meat extracts (Kutscher and Steudel, Zeitsch. physiol. Chem. 38, 101; Baur and Barschall, Chem. Zentr. 1906, ii. 1351; Einbeck, Zeitsch. physiol. Chem. 1913, 87, 145); in putrified meat (Wolff, Beitr. Chem. physiol. Path. 1903, 4, 254; Siegfried, Ber. 1895, 515). by the putrefaction of α -ketoglutaric acid (Nauberg and Ringer, Biochem. Zeitsch. 1915, 71, 237); in muscle, *see* D. M. Mayle (Bio-Chem. J. 1924, 18, 351; Chem. Soc. Abstr. 1924, 126, i. 791). According to Helm (Arch. Pharm. 1895, 233, 191), *succinite* (ordinary amber) contains succinic acid, but *gedanite* does not. Succinic acid is formed during various processes of fermentation. The succinic acid ferment is the name given to the microbe which develops in solutions of ammonium tartate and nutritive salts, converting them into the ammonium salts of carbonic, acetic, formic, and especially succinic acids. It is of no danger to the sugar manufacturers as their operations require a temperature of 60°, which kills it (Teixeira, Bied. Zentr. 1885, 493). In the fermentation of sugar by yeast, succinic acid is produced. It is formed not from the sugar, but by autolytic fermentation of the protein substance in the yeast cells, whereby glutamic acid is produced, and the latter is then converted into succinic acid (Kunz, J. Soc. Chem. Ind. 1907, 108; Ehrlich, Biochem. Zeitsch. 18, 391; Effront, Compt. rend. 119, 92). It is also formed by the bacteriological fermentation of asparagine (Neuberg and Cappezzuoli, Biochem. Zeitsch. 18, 424); and the schizomycetic fermentation of malic acid through *Bacillus lactis aërogenes* or of tartaric acid through *Bacterium termo* (Emmerling, Ber. 1899, 1915; König, *ibid.* 1881, 211). It is formed from aldehydopropionic acid by enzymatic reactions (Neuberg and Ringer, Biochem. Zeitsch. 1918, 91, 131). Succinic acid is formed by the oxidation of fats (Bouveault, Bull. Soc. chim. 19, [iii.] 562), of stearic acid (Bromeis, Annalen, 35, 90; 37, 292), Japanese wax (Sthamer, *ibid.* 43, 346), beeswax (Ronalds, *ibid.* 43, 356), spermaceti (Radcliff, *ibid.* 43, 351), sebacic and azelaic acids (Arppe, *ibid.* 95, 242; J. 1864, 377), camphor (Bredt, Ber.

1894, 2093), and of camphene (Marsh and Gardner, Chem. Soc. Trans. 1896, 84). Harries (Ber. 1904, 2708) has obtained succinic acid from rubber through fission with ozone. For methods of separating and purifying succinic acid from the commonly occurring organic acids, *v.* Schoorl, Zeitsch. angew. Chem. 1900, 367.

Succinic acid is prepared by the reduction of malic or tartaric acids with hydriodic acid (Schmitt, Annalen, 114, 106; Dessaignes, *ibid.* 115, 120); of fumaric and maleic acid with sodium amalgam (Kekulé, *ibid.* Spl. 1, 133) or with colloidal platinum (Paal and Gerum, Ber. 1908, 2273); by treating ethylene cyanide with acids or alkalis (Simpson, Annalen, 118, 375); by treating the ethyl ester of β -chloropropionic acid with potassium cyanide and hydrolysing the ester thus formed (Wichelhaus, Zeitsch. Chem. 1867, 247); by heating ethylenetricarboxylic acid at 160° (Bischoff, Ber. 1880, 2162); by reducing acetylenedicarboxylic acid with sodium amalgam (Bandrowsk, *ibid.* 1879, 2212); by the hydrolysis of ethyl ethylenetricarboxylate, obtained by the action of ethylsodiummalonate on ethylchloracetate (Bischoff and Kuhlberg, *ibid.* 1890, 634); by melting gum arabic, milk sugar (Hlasiwetz and Barth, Annalen, 138, 76) or carminic acid (Hlasiwetz and Grabowski, *ibid.* 141, 340) with caustic alkali; by treating bromacetic acid with silver powder at 130° (Steiner, Ber. 1874, 184); by the electrolysis of the potassium salt of the monoethyl ester of malonic acid and subsequent hydrolysis of the diethyl ester thus formed (Brown and Walker, Annalen, 261, 115); by oxidising aldehydopropionic acid with nitric acid (Perkin and Sprankling, Chem. Soc. Trans. 1899, 16); by treating the semi-aldehyde of maleic acid with sodium carbonate and potassium cyanide (Fecht, Ber. 1905, 1272); by condensing sodium ethylcyanacetate with formaldehydecyanhydrin and hydrolysing the product (Higson and Thorpe, Chem. Soc. Trans. 1906, 1460); by oxidising glutamic acid with hydrogen peroxide (Daking, J. Biol. Chem. 5, 409); or by heating with concentrated nitric acid and a trace of vanadic acid (Umetaró Suzuki and Yoshihiko Matsuyama, Japan. Pat. 39210); by oxidising furfural with Caro's acid (Cross, Bevan, and Briggs, Ber. 1900, 3132); by treating pyrrole with potassium hydroxide and hydroxylamine whereby the dioxime of succinic acid results (Zanetti, Atti R. Accad. Lincei. 1891, i. 344); by the action of hydrogen peroxide upon an aqueous solution of sodium butyrate at 65° (Cahen and Hurlley, Bio-Chem. J. 1917, ii. 164).

Properties.—Succinic acid crystallises in colourless monoclinic columns; melts at 182.7° (Reissert, Ber. 1890, 2244), at 185° (corr.) (Davidoff, *ibid.* 1886, 407), and boils at 261° (Krafft and Noerdlinger, *ibid.* 1889, 816), at 278.3° (corr.) (Bischoff and Kuhlberg, *ibid.* 1890, 634), and by heating strongly is converted into succinic anhydride; sp.gr. 1.554 (Tanatar and Tschelcbieff, J. Russ. Phys. Chem. Soc. 1892, 22, 549), 1.562 (Marshall and Cameron, Chem. Soc. Trans. 1907, 1522). Solubility in water (Lamouroux, Compt. rend. 128, 998): 100 c.c. dissolve—

Temp.	0°	15°	20°	35°	50°	65°
Grms. acid	2.79	4.9	5.8	10.6	18.0	28.1

or, according to Marshall and Cameron (Chem.

Soc. Trans. 1907, 1522), 100 grms. of water dissolve—

Temp.	0°	20°	25°	40°
Grms. acid	2.77	6.84	8.59	14.86

At 15°, 100 parts of dry ether dissolve 1.193 parts, 96 p.c. alcohol 9.986 parts, methyl alcohol 15.73 parts, and acetone 5.544 parts of succinic acid (Rau, Zeitsch. anal. Chem. 32, 483).

By heating succinic acid to a high temperature, under the action of atmospheric oxygen, it changes into carbon dioxide and water (de Coninck, Bull. Acad. Roy. Belgique, 1903, 633); heating with glycerol gives rise to acrolein and some acrylic acid (de Coninck and Raynaud, Compt. rend. 135, 1351), and fusing with caustic alkali decomposes it into oxalic and acetic acids. By the distillation of the dry calcium salt, diketohexamethylene is obtained in small quantity (Feist, Ber. 1895, 738), and also cyclopentanone and furfuran (Metzner and Vorländer, *ibid.* 1897, 1885). Hanriot (Compt. rend. 101, 1156) states that by distilling the acid with excess of quicklime, ethane and carbon dioxide are obtained. By the electrolysis of a solution of the potassium salt, ethylene and carbon dioxide are the chief products (Petersen, Chem. Zentr. 1897, ii. 519). In acid solution, succinic acid is scarcely acted on by potassium permanganate (Perdrix, Bull. Soc. chim. 23, [iii.] 645); electrolytic oxidation converts it into tartaric and oxalic acids, carbon monoxide and dioxide, methane and ethylene (Clarke and Smith, J. Amer. Chem. Soc. 1899, 967), whilst hydrogen peroxide yields tartaric acid (Zinns, Mon. Scient. 16, ii. 493). Fittig and his co-workers have studied the condensations of aldehydes and sodium succinate in the presence of acetic anhydride. Acetaldehyde and its higher homologues, chloral and benzaldehyde, yield substituted paraconic acids (Annalen, 255, 18, 43, 56, 68, 96, 97, 142; Stobbe and Kloeppel, Ber. 1894, 2407), salicylaldehyde yields dicoumarin (Fittig and Politis, Annalen, 255, 275), anisaldehyde and cinnamaldehyde yield substituted isocrotonic acids (Fittig, *ibid.* 255, 293; 331, 151), whilst furfuraldehyde yields $\alpha\gamma$ -difurfurylidene propionic acid and difurfurylidene succinic anhydride (Titherley and Spencer, Chem. Soc. Trans. 1904, 183; *v.* also Fichter and Scheuermann, Ber. 1901, 1626). Stobbe has studied the condensations which ethyl succinate undergoes with ketones in the presence of sodium methoxide. In this way $\gamma\gamma$ -disubstituted itaconic acids and γ -alkylenepyrro-tartaric acids are produced, the latter chiefly from ketones which contain a methylene group near the carbonyl group, and the former from ketones not containing a methylene group. Condensations have been effected with benzophenone, benzil, benzoin, cyclic ketones, &c. (Stobbe, Annalen, 308, 67 *et seq.*; 314, 111; 321, 94, 105; Ber. 1895, 1122, 3192; 1899, 3354; 1904, 2232). The esters of succinic and cinnamic acids condense to form β -phenylbutane- $\alpha\gamma\delta$ -tricarboxylic acid (Stobbe and Fischer, Annalen, 315, 232), whilst ethyl succinate condenses with valerolactone in the presence of sodium methoxide to form valactenesuccinic anhydride and valactenepropionic acid (Fittig, Salomon and Wernher, *ibid.* 331, 191). By heating succinic acid, acetic

anhydride, anhydrous sodium acetate and zinc chloride, and distilling the residue in steam furfuran is obtained (Magnanini and Benti-voglio, Gazz. chim. ital. 24, i. 433) and on distillation of sodium succinate with phosphorus pentasulphide, thiophen is obtained. A mixture of mono- and dibromo-succinic acids is obtained by heating succinic acid, phosphorus and bromine in a sealed tube (Gorodetzky and Hell, Ber. 1888, 1730; Volhard, Annalen, 242, 141; Auwers and Imhäuser, Ber. 1891, 2233). *r*- $\alpha\beta$ -dibromo-succinic acid is obtained by addition of bromine to maleic acid or maleic anhydride, whilst *meso*- $\alpha\beta$ -dibromo-succinic acid is formed by direct bromination of succinic acid. For the resolution of the former acid, *see* Holmberg, Svensk. Kem. Tidskr. No. 5, 1911; *ibid.* 1921; McKenzie, Chem. Soc. Trans. 1912, 101, 1196. For the action of magnesium, *see* Zalkind, J. Russ. Phys. Chem. Soc. 1914, 46, 688. Inactive bromosuccinic acid and *l*-bromosuccinic acid react with sodium iodide in acetone solution forming inactive *iodosuccinic acid* (Westerlund, Ber. 1915, 48, 1179). By heating barium succinate with sodium methoxide, propionic acid is produced (Mai, *ibid.* 1889, 2136; *v.* also Holbe, Annalen, 119, 173), and by heating the ethyl ester at 400° with alumina, tetrahydroquinone is produced (Bull. Soc. chim. [iv.] 5, 480). Ethyl succinate reacts with alkyl iodides in the presence of zinc to form $\gamma\gamma$ -dialkylbutyrolactones (Kasansky, Chem. Soc. Abstr. 1904, i. 367); with magnesium phenyl bromide to form tetraphenyltetramethylene oxide (Acree, Amer. Chem. J. 1905, 33, 180); and with hydroxylamine hydrochloride and sodium hydroxide and subsequent treatment with acetic anhydride to form succinylhydroxamic acid (Hantzsch and Urbahn, Ber. 1895, 74). Electrolysis of molecular proportions of ethyl succinate and ethyl malonate gives rise to glutaric and adipic acids (Vanzetti and Coppadoro, Atti R. Accad. Lincei, 1903, 12, ii. 209).

Succinic acid and its alkyl derivatives when heated break down into anhydrides and water. The anhydride formation takes place more readily if the hydrogen atoms of the ethylene residue of succinic acid are replaced by alkyl groups (Auwers and Meyer, Ber. 1890, 101). The alkyl-succinic acids form anhydrides more readily with acetyl chloride and are more volatile in steam than their isomeric alkyl-*n*-glutaric acids (Auwers, Annalen, 285, 212). Anilic acids are produced by adding amines to the anhydride in chloroform, ether or benzene, and these on treatment with acetyl chloride or phosphorus pentachloride or by the action of heat alone yield anils.

Literature.—*Alkyl-succinic acids*, Bischoff, Ber. 1891, 1064 *et seq.*; 1890, 631; Auwers, Annalen, 285, 212; 292, 132, 152; 298, 147 *et seq.*; Bone, Chem. Soc. Proc. 1899, 5; Bone and Sprankling, Chem. Soc. Trans. 1899, 839; 1900, 654, 1298. *Dissociation constants of acids*, Bone and Sprankling, Chem. Soc. Proc. 1900, 184. *Arylsuccinic acids*, Avery and Upson, J. Amer. Chem. Soc. 30, 600. *Anhydrides*, Bischoff, Ber. 1890, 620, 656; Auwers and Meyer, *l.c.* *Anils and anilic acids*, Auwers, Oswald and Thorpe, Annalen, 285, 226; Auwers, *ibid.* 285, 229; 292, 132, 194; 309, 316. *Imides*, Miolati, Atti R. Accad. Lincei, 1894, i. 515;

Koller, Ber. 1904, 1598. *Esters*, Bone, Sudborough and Sprankling, Chem. Soc. Trans. 1904, 534.

Succinic acid may be used as a standard in alkalimetry, acidimetry and iodimetry (Phelps, Hubbard and Weed, Amer. J. Sci. 23, 211; 24, 194; 26, 143; cf. Peters and Sauchelli, *ibid.* 1916, [iv.] 41, 244). For this purpose the acid is prepared by the hydrolysis of the pure ester, obtained by passing alcohol vapour charged with pure hydrogen chloride into a mixture of succinic acid, alcohol and hydrogen chloride, together with the addition of a little pure fused zinc chloride, and distilling continuously at 100°–110°; *v.* also ACIDIMETRY and ALKALIMETRY. The succinates of the rare earths of the yttrium group are of importance, as it is by their fractional crystallisation that these elements may be separated from each other (Lenher, J. Amer. Chem. Soc. 30, 572).

Detection and Estimation.—Succinic acid does not char on the addition of sulphuric acid in the cold, but on warming darkens, sulphur dioxide being evolved. Silver nitrate gives a white precipitate in neutral solutions, soluble in ammonia; calcium chloride, a white precipitate on standing; and ferric chloride, a yellowish-brown precipitate; *v.* also Neuberg, Zeitsch. physiol. Chem. 31, 574. Succinic acid may be estimated in the presence of tartaric and lactic acids by the method of Bordas, Joulin and Raczkowski (J. Pharm. Chim. 1898, 7, 417; Chem. News, 78, 18). The solution containing the acids is exactly neutralised with *N*/10 potassium hydroxide, excess of silver nitrate solution is added, and the precipitate washed until the filtrate no longer gives a precipitate with potassium chromate. The precipitate, which consists of silver succinate, is washed back into the flask with water, one or two drops of potassium chromate solution added, and then sodium chloride solution is run in until the red colour disappears. The solution is then titrated back with *N*/10 silver nitrate solution (*v.* also Makowka, Chem. Zentr. 1908, i. 2207). *Estimation in presence of citric and tartaric acids*, *v.* Micko, Zeitsch. anal. Chem. 31, 465. *Estimation in plants*, *v.* Jörgensen, Chem. Zentr. 1907, i. 1224. *In wines and fermented liquids*, *v.* Laborde and Moreau, Ann. Inst. Pasteur, 1899, 13, 657; Kunz, Chem. Soc. Abstr. 1903, ii. 701; Muller, Bull. Soc. chim. [iii.] 15, 1203; Mestrezat, Compt. rend. 143, 185; Albaharz, *ibid.* 144, 1232; Prandi, Chem. Zentr. 1905, ii. 992; Pozzi-Escot, Compt. rend. 147, 600; Heiduschka and Quincke, Arch. Pharm. 245, 485; Blumenthal, Virchow's Archiv. 137, 539; Schmitt and Hupi, Reb. intern. falsific. 10, 199; Rau, Zeitsch. anal. Chem. 32, 482; Von der Heide and Steiner, Chem. Soc. Abstr. 1909, ii. 444; Von der Heide and Schwenk, *ibid.* 1912, ii. 1005; Grey, Ann. Chim. anal. 1918, 23, 143; Analyst, 1918, 357; Dutoil and Duboux, Bull. Soc. Chim. 1913, [iv.] 13, 832.

Salts. $\text{KHC}_4\text{H}_4\text{O}_4 \cdot 2\text{H}_2\text{O}$; $\text{KHC}_4\text{H}_4\text{O}_4$; $\text{KH}_3(\text{C}_4\text{H}_4\text{O}_4)_2$ (Marshall and Cameron, Chem. Soc. Trans. 1907, 1514); $\text{NaHC}_4\text{H}_4\text{O}_4$; $\text{Na}_2\text{C}_4\text{H}_4\text{O}_4 \cdot 6\text{H}_2\text{O}$ (Rammelsberg, J. 1855, 467; Minio, Zeit. Kryst. 31, 415);

$\text{CaC}_4\text{H}_4\text{O}_4 \cdot \text{H}_2\text{O}$; $\text{CaC}_4\text{H}_4\text{O}_4 \cdot 3\text{H}_2\text{O}$ (Milojkovic, Monatsh. 14, 699); salts of the rare earths (Meyer, Zeitsch. anorg. Chem. 33,

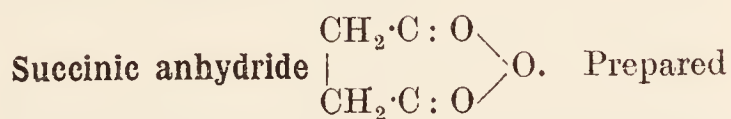
31, 113; Morgan and Cahen, Pharm. J. 24, [iv.] 428; Tanatar and Kurowski, J. Russ. Phys. Chem. Soc. 39, 936); double potassium salts (Reynolds, Chem. Soc. Trans. 1898, 701). Uranium salt $\text{UO} \cdot \text{C}_4\text{H}_4\text{O}_4 \cdot 2\text{H}_2\text{O}$ (Mazzucchelli and Greco d'Alceo, Atti R. Accad. Lincei, 1912, [v.] 21, ii. 620. Uranyl succinate



(Courtois, Compt. rend. 1914, 158, 1688). Solubilities of salts of succinic acid, *v.* Partheil, Arch. Pharm. 241, 412; Cantoni and Diotallevi, Bull. Soc. chim. [iii.] 33, 27.

Esters. For velocity of esterification of succinic acid, see Kailan, Zeitsch. physikal. Chem. 1915, 89, 676. The *dimethyl ester* is a crystalline solid, m.p. 19°; b.p. 195.3° (corr.); sp.gr. 1.1207 at 20°/4° (Emery, Ber. 1889, 3185). It may be prepared by the interaction of methyl bromacetate and magnesium (Spencer and Crewsdon, Chem. Soc. Trans. 1908, 1826). The *diethyl ester* is a liquid, b.p. 216.5° (corr.), sp.gr. 1.04645 at 15° (Perkin, *ibid.* 1884, 515). For preparation, *v. supra* (Phelps and Hubbard). *Ethylene ester*, m.p. 88°–90°; sp.gr. 1.345 at 17°. Prepared from succinic acid and glycol or from ethylene dibromide and silver succinate (Vorländer, Annalen, 280, 177). *Aryl esters*, *v.* Bischoff and Hedenström, Ber. 1902, 4073 *et seq.* *Isobornyl ester*, *v.* Beckmann, *ibid.* 1907, 485. *Menthyl ester*, *v.* Hilditch, Chem. Soc. Trans. 1909, 1580. *Sanatyl esters*, *v.* Riedel, D. R. P. 208637; Chem. Zentr. 1909, i. 1442; Kalle and Co., D. R. P. 201639; Chem. Zentr. 1908, ii. 994. *Dibenzyl ester*, white crystalline odourless powder, soluble in alcohol, ether, chloroform and in the fixed oils; used in medicine. The two inactive dichloro-succinic acids give ethyl and methyl esters.

Succinyl chloride $\text{C}_4\text{H}_4\text{O}_2\text{Cl}_2$. Prepared from succinic acid and phosphorus pentachloride (Gerhardt and Chiozza, Annalen, 87, 293; Möller, J. pr. Chem. [ii.] 22, 208); m.p. 16°–17° (20° Morrell), b.p. 190°–192° (corr.) (Vorländer, Annalen, 280, 183; Perkin, Chem. Soc. Trans. 1888, 563). It is a mixture of symmetrical and asymmetrical compounds (Vorländer, Ber. 1897, 2268; Meyer and Marx, *ibid.* 1908, 2459; Auger, Ann. Chim. 1891, [vi.] 22, 320.



by heating the acid alone or with phosphorus pentoxide, acetyl chloride, acetic anhydride or benzoyl chloride (Gerhardt and Chiozza, Annalen, 87, 293; Blaise, Bull. Soc. chim. [iii.] 21, 643; Anschütz, Ber. 1877, 1833; Schulz, *ibid.* 1885, 2459); by treating the acid with phosphorus pentoxide in toluene solution (Bakunin, Gazz. chim. ital. 30, ii. 340); by treating sodium succinate in neutral or feebly alkaline solution with acetic anhydride (Oddo and Manuelli, *ibid.* 26, ii. 482). White solid, m.p. 119.6°; b.p. 261°; sp.gr. 1.1036 at 20°/4°: purified by recrystallisation from chloroform (Negri, *ibid.* 26, i. 77). Hydroxylamine hydrochloride reacts with the anhydride to form succinylhydroxamic acid which may be isolated by means of its barium salt (Errera, *ibid.* 25, ii. 25). Pyrogallol condenses with the anhydride to give pyrogallol-succinin, a dyestuff giving reddish-brown

shades with alumina mordants (Georgievics, Monatsh. 20, 450); hydroquinone undergoes a similar condensation (Meyer and Witte, Ber. 1908, 2457). Reduction with sodium amalgam and hydrochloric acid yields butyrolactone. Succinic anhydride condenses with *m*-aminophenols to form succinin-dyestuffs which are similar to the rhodamines (Bayer and Co., D. R. P. 51983; Frdl. ii. 86); with 1·8-naphthylenediamine it yields a dyestuff, green in acid solution (Bayer and Co., D. R. P. 202354; Chem. Zentr. 1908, ii. 1397) (*v.* TRIPHENYL-METHANE COLOURING MATTERS).

Succinic peroxide $C_4H_4O_4$ and *persuccinic acid* are formed by the action of hydrogen peroxide on the anhydride (Clove and Houghton, Amer. Chem. J. 1904, 32, 43; *v.* also Vanino and Thiele, Ber. 1896, 1724).

Succinimide. Prepared by heating succinic acid with ethylene cyanide (König, J. pr. Chem. 69, [ii.] 1; Miller, J. Amer. Chem. Soc. 16, 433); by distilling ammonium acetate (Landsberg, Annalen, 215, 173); by the interaction of succinonitrile and benzoic acid (Matthews, J. Amer. Chem. Soc. 1898, 650); by the partial hydrolysis of succinonitrile with sulphuric acid (Bogert and Eccles, *ibid.* 1902, 20); by heating acetonitrile with succinic acid (Miller, *l.c.*); by the action of ammonia on succinic anhydride (D'Arcet, Annalen, 16, 215); by distilling a mixture of succinic anhydride and carbimide (Dunlap, J. Amer. Chem. Soc. 18, 332). M.p. 125°–126°; b.p. 287°–288° (Menschutkin, Annalen, 162, 166). Phosphorus pentachloride reacts with succinimide to form tetrachloropyrrole, which is converted into pyrrole by treatment with zinc-dust and caustic potash (Ciamician and Silber, Ber. 1883, 2398). By electrolytic reduction in sulphuric acid, pyrrolidine is produced (Tafel and Stern, *ibid.* 1900, 2224; Zeitsch. physikal. Chem. 54, 443), whilst electrolysis of an aqueous solution yields succinic acid and ammonia (Pannain, Gazz. chim. ital. 35, ii. 94). Reduction with sodium amalgam and hydrochloric acid yields butyrolactone (Fichter and Herbrand, Ber. 1896, 1192); ammonia gas converts succinimide at –10° into succinamide (Roubtsoff, Chem. Soc. Abstr. 1886, 141); potassium hypobromite converts it into β -aminopropionic acid (Hoogewerff and van Dorp, Rec. trav. chim. 10, 4). Crystalline compounds with phenols (*ibid.* 1900, 19, 32); compound of silver succinimide with hexamethylenetetramine (D. R. P. 217897; Chem. Zentr. 1910, i. 701). The hydrogen atom of the imino group is capable of replacement by metals and organic radicles. For substituted alkyl-succinimides *v.* Meister, Lucius and Bruning, Eng. Pats. 15327, 15328; J. Soc. Chem. Ind. 1894, 800. The metallic derivatives of succinimide are of importance, as when dissolved in water and warmed, colloidal solutions of the metallic oxides are obtained in many cases. *Copper succinimide* (Tschugaeff, Ber. 1905, 2899; Ley, *ibid.* 1905, 2199; Ley and Werner, *ibid.* 1906, 2177). *Silver succinimide* (Ley and Schaeffer, *ibid.* 1906, 1259; Ley and Werner, *ibid.* 1913, 4040). *Nickel succinimide* (Tschugaeff, *ibid.* 1906, 3190). Complex metallic derivatives (Tschugaeff, *ibid.* 1907, 1973).

Succinimide potassium periodide



m.p. 141°–149°, light brown crystals (Clover, J. Amer. Chem. Soc. 1920, 42, 1248).

Succinanil and Succinanilide *v.* Dunlap and Cummer, J. Amer. Chem. Soc. 25, 612; Morrell, Chem. Soc. Trans, 1914, 105, 2702.

Succinamide, m.p. 242°–243°, *v.* Henry, J. 1885, 1333; Morrell, *l.c.* For the crystalline structure of succinic acid, succinic anhydride, and succinamide, *see* K. Yardley (Proc. Roy. Soc. 1924, 105, 451).

Aminosuccinic acid *v.* ASPARAGINE.

Succinmonohydrazide $C_4H_{10}O_4N_2$, a white crystalline substance. Cyclic *succinhydrazide* $(CHON)_n$ dissolves in alkalis, reduces Barreswil's (Fehling's) solution, and gives with ammoniacal silver nitrate an unstable white precipitate, together with metallic silver. It is slowly hydrolysed by prolonged boiling with dilute hydrochloric acid, forming hydrazine and oxalic acid (Sernagiotto and Paravagno, Gazz. chim. ital. 1914, 44, i. 538).

For hydrazides and azoimides of succinic acid, *see* Curtius and collaborators, J. pr. Chem. 1915, [ii.] 92, 74.

*iso***Succinic acid.** *Methylmalonic acid*



Prepared by treating α -cyanopropionic acid with potash (Wichelhaus, Zeitsch. Chem. 1867, 247); by the action of potassium cyanide on the potassium salt of α -bromopropionic acid (Lassar Cohn, Annalen, 251, 349) or on ethyl α -bromopropionate (Pusch, Arch. Pharm. 232, 186; Byk, J. pr. Chem. ii. 1, 19); by the dry distillation of the esters of methyloxalacetic acid (Wislicenus and Kiesewetter, Ber. 1894, 796); by boiling silver cyanoform with water, isolating the nitrile and hydrolysing the latter with sodium hydroxide (Hantzsch and Osswald, *ibid.* 1899, 648).

Properties.—Crystallises in colourless prisms, m.p. 135° (W. and K.); sp.gr. 1·455 (Tanatar and Tchelebieff, J. Russ. Phys. Chem. Soc. 22, 548). For solubility in water (Massol and Lamouroux, Compt. rend. 128, 1000): 100 c.c. dissolve

Temp.	0°	25°	50°
Grms. acid . . .	44·3	67·9	91·5

Readily soluble in alcohol, ether, and acetic acid. Electrolysis of an aqueous solution of the acid yields acetaldehyde, ethylene, carbon dioxide, carbon monoxide, oxygen and hydrogen (Petersen, Chem. Zentr. 1897, ii. 519; Zeitsch. physikal. Chem. 33, 698; *cf.* Lassar Cohn, Annalen, 251, 349). Potassium permanganate oxidises it to acetic acid, carbon dioxide and water (Perdrix, Bull. Soc. chim. ii. 23, 645); nitric acid converts it into carbon dioxide, acetic acid and trinitromethane (Franchimont, Rec. trav. chim. 5, 281). The potassium salt of the monomethyl ester yields on electrolysis the diethyl esters of the two symmetrical dimethylsuccinic acids (Brown and Walker, Annalen, 274, 42). Ethylsodiomethylmalonate condenses with ethyl α -bromobutyrate to form symmetrical methylethylsuccinic acid (Auwers, Annalen, 298, 147); with ethyl α -bromoisobutyrate to form *aa*-dimethylglutaric and trimethylsuccinic acids (Auwers and Jackson, Ber. 1890, 1611; Bischoff, *ibid.* 1891, 1046; Auwers and Köbner, *ibid.* 1891, 1929); with ethyl γ -chlorobutyrate to form α -methyladipic

acid and β -dimethylglutaric acid (Montemartini, *ibid.* 1896, 2058; Gazz. chim. ital. 26, ii. 259; cf. Bone and Sprankling, Chem. Soc. Trans. 1899, 849); with ethyl β -iodopropionate to form α -methylglutaric acid (Auwers and Titherley, Annalen, 292, 209); with ethyl- α -bromoisovalerate in alcoholic solution to form *cis*-methylisopropylsuccinic acid and in xylene solution to form a mixture of *cis*- and *trans*-methylisopropylsuccinic acids (Bentley, Perkin and Thorpe, Chem. Soc. Trans. 1896, 270); with esters of unsaturated acids to form esters containing a four carbon atom ring (Michael, Ber. 1900, 3731; Svoboda, Monatsh. 1902, 842).

Dimethyl ester.—Colourless liquid, b.p. 178° – 179.5° (770 mm.).

Diethyl ester.—Prepared from diethyl sodio-malonic ester and methyl iodide (Perkin, Chem. Soc. Trans. 1896, 1476; Michael, J. pr. Chem. ii. 72, 537); colourless liquid, b.p. 198.5° – 199° at 765 mm. (corr.).

Methylmalonamide $\text{CH}_3\cdot\text{CH} < \begin{smallmatrix} \text{CONH}_2 \\ \text{CONH}_2 \end{smallmatrix}$. Pre-

pared from malonamide, methyl iodide, sodium methoxide and methyl alcohol, or from methylmalonyl chloride and aqueous ammonia (Meyer and Bock, Annalen, 347, 104); m.p. 212° (Conrad and Schulze, Ber. 1909, 730). The *anilide* melts at 214° (Comanducci and Lobello, Chem. Soc. Abstr. 1905, i. 271; 1907, i. 409).

Amino-methylmalonic acid *v.* ASPARAGINE.

SUCCINITE *v.* AMBER.

SUCRAMINE. The ammonium salt of saccharin: known also as 'Lyons sugar.'

SUGAR (Fr. *sucre*; Ger. *Zucker*) is the generic name for a group of bodies belonging to the class of compounds known as carbohydrates, which occurs naturally in the vegetable or animal kingdoms, or may, in some cases, be formed synthetically.

The sugars in general possess a more or less sweet taste, are crystallisable, are readily soluble in water, less soluble and in some cases insoluble in alcohol, and are insoluble in ether and similar solvents immiscible with water. They are optically active, *i.e.* their solutions rotate the plane of polarised light to the right or left; whilst some precipitate cuprous oxide from Fehling's Barreswil's solution, an alkaline solution of cupric sodium tartrate. Another important property of some sugars is their behaviour towards phenylhydrazine, insoluble compounds being formed, a reaction which proves of much value in special cases of differentiation. Then certain of the sugars undergo alcoholic fermentation with yeast, and behave in a characteristic manner with mineral acids, both dilute and concentrated. Each individual member of the sugar group may be considered either as an aldehyde or as a ketone of hexatomic alcohols, the first being termed aldoses, and the latter ketoses. The sugars are divided into three groups: (1) Mono-saccharides, which may be further subdivided into bioses, trioses, hexoses, &c., according to the number of carbon atoms they contain. The hexoses have the formula $\text{C}_6\text{H}_{12}\text{O}_6$, and include dextrose (glucose, grape sugar, or starch sugar), mannose, galactose, lævulose (fructose, honey sugar, or fruit sugar), sorbose, arabinose, and xylose. (2) Di-saccharides, having the formula $\text{C}_{12}\text{H}_{22}\text{O}_{11}$, which

may be considered as composed of two mono-saccharide residues, less a molecule of water. This group includes sucrose or saccharose (cane sugar, beet sugar); lactose (milk sugar); maltose, and melibiose. (3) Tri-saccharides, which have the formula $\text{C}_{18}\text{H}_{32}\text{O}_{16}$, the best known member of which is raffinose (melitriose or gossypose) (*v.* CARBOHYDRATES).

Although extracted from different plants, such as the sugar cane and beet, commercial sugar consists essentially of sucrose or saccharose, admixed with very small quantities of other sugars, such as glucose and fructose in cane sugar, and, in addition to these, traces of raffinose in beet sugar, together with traces of organic and mineral impurities. The purity of commercial cane and beet sugars is therefore measured by the percentage of contained sucrose, whilst any differences in colour, odour, and flavour are due to the impurities present. In refined sugar, these impurities are almost completely eliminated, and the percentage of sucrose rises to about 99.8 p.c. In this purified condition cane and beet sugars possess identical sweetening powers, and are indistinguishable by chemical analysis. The properties of sucrose and the methods of extracting and refining it form the subject of this article.

Properties of sucrose, saccharose, or cane sugar.—The disaccharide sucrose crystallises from its pure aqueous solution in the monoclinic system. When pure, it has a sp.gr. of 1.589 at 15° . It is freely soluble in water, in direct proportion to the temperature; a saturated aqueous solution at 15.5° contains 66 p.c. of sugar and has a sp.gr. of 1.326. It is sparingly soluble in absolute alcohol, its solubility in this medium increasing with the amount of water present. On very slowly evaporating an aqueous solution of sucrose, large crystals of 'sugar candy' are produced. The rapidity of crystallisation is influenced not only by the concentration and temperature of the solution, but also by the nature and amount of the foreign substances present, reducing sugars, certain salts, and organic non-sugar bodies having an inhibitive effect.

According to E. O. von Lippman (Ber. 1924, 57, 256) *d*-arginine, *d*-lysine, *l*-histidine, pyrrolidine- α -carboxylic acid (proline), skatolecarboxylic acid, and *l*-cystine have been isolated from the liquors remaining after desaccharification of beet molasses. *l*-Phenylalanine, a substance $\text{C}_{18}\text{H}_{20}\text{O}_5\text{N}_2$, probably tyrosine anhydride, and a compound $\text{C}_6\text{H}_7\text{O}_4\text{N}$, probably the imide of tricarballic acid (*cf.* Thole and Thorpe, Chem. Soc. Trans. 1911, 99, 1688), are present in the juice of freshly-harvested but still unripe beetroot (J. Soc. Chem. Ind. 1924, 43, B. 270).

Sucrose rotates the plane of polarised light to the right, its specific rotatory power being $[\alpha]_D^{20} 66.5$. When heated alone it melts at 185° – 186° (Burne, Chem. News, 1914, 110, 47), but in presence even of traces of water it is decomposed at temperatures above 100° , when a dark-coloured mixture of various bodies collectively termed 'caramel' results. Heated under reduced pressure it yields *l*-glucosan, furfuraldehyde and its derivatives, acetic acid, formaldehyde together with carbon dioxide, carbon monoxide and unsaturated hydrocarbons

(Reilly, J. Soc. Chem. Ind. 1921, 40, 249 T). Treatment with dilute mineral acids, or with the enzyme *invertase*, hydrolyses sucrose to a mixture of equal parts of dextrose and lævulose (invert sugar), a contraction in volume occurring, but if concentrated mineral acids be employed decomposition occurs. Heated with strong nitric acid (sp.gr. 1.41) to 72°–75°, it yields a mixture of oxalic acid and mesoxalic acid, the latter of which may be readily separated from the solution as the sparingly soluble sodium mesoxalate $C(OH)_2(CO_2Na)_2$ (Chattaway and Harris, Chem. Soc. Trans. 1922, 121, 2703; cf. Kiliani, Ber. 1922, 55, [B.] 2817). Sucrose is also inverted by the action of radium emanation (Fernau, Biochem. Zeitsch. 1920, 102, 246). Sucrose is capable of uniting with alkalis and alkaline earths, to form sucrates or saccharates, the most important of which are the calcium, barium, and strontium compounds. The mono- and di-basic calcium saccharates are soluble in water, but the tri-basic compound is insoluble. On passing carbon dioxide slowly into a fine suspension of tri-basic calcium saccharate in water, the sucrose is liberated and calcium carbonate precipitated. With salts, such as the alkali chlorides and nitrates, sucrose also forms double compounds. On mixing sucrose with an alcoholic solution of α -naphthol in presence of sulphuric acid, a characteristic purple colour appears, a reaction that is extremely delicate, and for this reason much used for detecting traces of sugar in very dilute solution.

Occurrence of sucrose.—Sucrose is found most abundantly in the sugar beetroot (*Beta vulgaris* [Linn.]), in the sugar cane (*Saccharum officinarum* [Linn.]), in sorghum (*Sorghum vulgare* [Pers.]), in maize (*Zea Mays* [Linn.]), in the maple (*Acer saccharinum* [Wangenh.]), and in certain palms (such as *Caryotaurens Nipa fruticans*, *Borassus flabellifer* [Linn.], *Cocos nucifera* [Linn.], and *Avenga saccharifera* [Labill.]). It is also present in the sap of nearly all the higher plants: but only a few of these contain it in sufficiently large amount, and in a pure enough state to permit of its profitable extraction.

Production of sugar for consumption.—The sugar consumed in civilised countries is obtained, almost entirely, from (1) the sugar beetroot, and (2) the sugar cane. A small proportion of the world's production of sugar is also derived from the maple and palm trees, and from sorghum.

Sugars are formed in the leaf of plants under the influence of sunlight, and by the agency of the green colouring matter—chlorophyll—present in the leaf. The carbon of sugar is derived from carbon dioxide gas, present in the atmosphere, the hydrogen and oxygen being derived from water entering the plant from the soil, but previously existing as water vapour in the atmosphere. Thus, the three elementary constituents of sucrose are indirectly derived from the atmosphere, whereas the plant itself also abstracts mineral elements from the soil. When formed, sucrose is in the state of solution in the sap, and passes out of the leaf into other parts of the plant, where it can be stored until the plant can make further use of it. Thus it is stored in the stem of the sugar cane, but in the tap-root of the beet.

(1) **The sugar beetroot** (*Beta vulgaris*) is a hardy biennial plant, long under cultivation in

France, Germany, Austria, Russia, Holland, Belgium, Norway, Sweden, Denmark, Italy, Spain, and more recently introduced into the United States, Canada, Australia, New Zealand, South Africa, and Great Britain.

From the original Silesian white beet, the Vilmorin and the Wanzleben types have been derived, and from these a great number of varieties, differing not only in the shape of the root but also in the form and size of the leaves, have been created by the different seed growers. Of these may be mentioned Wohanka's 'W.E.R.' and 'W.Z.R.'; Dippe's 'Best'; Aderstedter's 'A,' 'B,' and 'C'; and the various Désprez, Simon-Legrand, Knauer, and Jules-Roberts varieties.

The sugar beet is rather long and conical (see Fig. 1); it is regular and not forked, and does not throw out 'fingers and toes.' Its flesh is firm, not very soft, yields juice only under pressure, and its colour may be white, rose, or



FIG. 1.

grey. The root, without its leaves, may weigh between 1 and 2 lbs., according to the variety and the conditions of climate and cultivation.

By means of scientific cultivation and seed-selection, the sugar content of the beetroot has been raised during the past fifty years from 10 to 20 p.c. or more, but 16 p.c. is a general average.

(2) **The sugar cane** is a gigantic grass, and belongs to the natural order *Gramineæ*, the tribe *Andropogoneæ*, and the genus *Saccharum*.

The stem is jointed and has a hard rind, or skin, varying in colour from pale yellow to deep purple, and sometimes striped. The interior of the stem consists of colourless parenchyma tissue in which the sweet juice is stored, but the nodes contain much more fibre and a less pure juice. Two nodes and the intervening smooth internode is called 'a joint.' A single leaf springs from each node and the base of the leaf encircles the joint to which it is attached. When the cane develops, the leaves attached to the lower and riper joints wither and fall, or are stripped off by hand. The cane plant then appears as in Fig. 2. Each joint also bears a bud or 'eye,' capable of developing into a shoot when a cutting of the stem is buried in the soil. This is the practical method of propagating the

plant on the sugar estate. Cuttings may be made from any portion of the stem, but as the uppermost joints are unsuitable for sugar manufacture, they are most economically employed as planting material. The cane ripens more rapidly in the tropics, but can be successfully cultivated in semi-tropical climates. Owing to its transportation from one country to another, numerous varieties have been produced by differences of soil and climate. These are called 'natural varieties,' and their distinctive characters have become permanent after continuous cultivation. No systematic classification of these natural varieties exists, but Deerr and Eckart have attempted to identify



FIG. 2.

certain main varieties, which have received entirely different names in different countries. For example (1) The Otaheite cane (which is stated to be identical with the Bourbon, Lahaina, Louzier, Keni-keni, Portii, and Cuban); (2) Cheribon canes, including the Yellow Violet, Purple Violet, the Transparent or Ribbon cane, and the Tibboo Batavee of the Straits Settlements; (3) Tanna canes, which may be striped, white, or black; and (4) the Salangore, Cavanerie, Uba and Bamboo canes.

Previous to 1885, it was believed that the sugar cane was incapable of producing fertile seeds; but, shortly after, Harrison and Bovell of Barbados demonstrated, not only that the cane produces fertile seeds, but also the possibility of producing new and improved varieties by this method of propagation. But, owing to

the great variability of the seedling from the character of the parent cane, it was soon found that the direct method of seed-selection, which had proved so successful in evolving the sugar beet, was quite inapplicable to the sugar cane, and a more laborious method had to be followed, which need not be described here. In Demerara alone, Prof. Harrison raised over a million seedling varieties, of which the great majority were entirely worthless, and only about one dozen gave promise of being suitable for cultivation on a large scale. These investigations are being continued in Demerara and other cane-producing countries. Each seedling variety is distinguished by the first letter in the name of the country where it was produced, followed by a number. For example, some of the Demerara seedling canes are: D 74, D 95, D 145, D 167, D 625; Barbados canes are B 208, B 6450; Java canes are J 36, J 139, J 213; and so on. The chemical composition of the cane varies considerably in different varieties and under different climatic conditions, but approximate figures are: sucrose, 11 to 16 p.c.; reducing sugars, 0.5 to 1.5 p.c.; fibre, 8 to 15 p.c.; organic non-sugar, 0.5 to 1.0 p.c.; and ash, 0.5 to 1.0 p.c. The reducing sugars consist of dextrose and lævulose, the former sugar generally predominating. Amongst the organic non-sugars are included (a) nitrogenous compounds as albumins, nucleins, albumoses, peptones, amines, amino acids, and (b) non-nitrogenous bodies, as cellulose, fat, wax, gum, chlorophyll, &c. In addition the following organic and inorganic acids and bases are found: malic, succinic, oxalic, glycollic, sulphuric, phosphoric and silicic acids; potash, soda, lime, magnesia, alumina, iron and manganese oxides.

Raw and refined sugars. The manufacture of white sugar formerly comprised two stages, which developed into distinct industries, namely, (1) the manufacture of raw sugar from the juice of the plant, and (2) the refining of this raw sugar to render it more suitable for consumption, or as raw material for certain industries. The finished product of the raw sugar factory thus becomes the raw material treated in the refinery, and the latter may be located in a country where neither the cane nor the beet are grown. White sugar is now produced in the raw sugar factory by methods to be described hereafter, and is termed 'plantation white' or 'plantation refined,' but is not correctly described as refined sugar. A superior quality of raw cane sugar, first made exclusively in Demerara, but now also manufactured in the West Indian Islands, is consumed without further treatment in the refinery. It has a fine yellow colour, due to the natural colouring matter of the cane, and a pleasant flavour. Fraudulent imitations of this sugar have been made by colouring white beet sugar with aniline dyes.

(a) MANUFACTURE OF RAW SUGAR FROM THE BEET.

Briefly stated, the operations involved in the manufacture of sugar from the beetroot are as follows: (1) extraction of the juice; (2) chemical treatment of the juice; (3) concentration of the juice to syrup; (4) crystallisation of the sugar from the syrup; (5) separation of the

crystals; and (6) treatment of the separated syrup and the working-up of the after-products.

(1) *Extraction of the juice from the beetroot.*—On arriving in the neighbourhood of the factory, the roots are placed in heaps or silos, to be there stored until they can be treated, and are thence

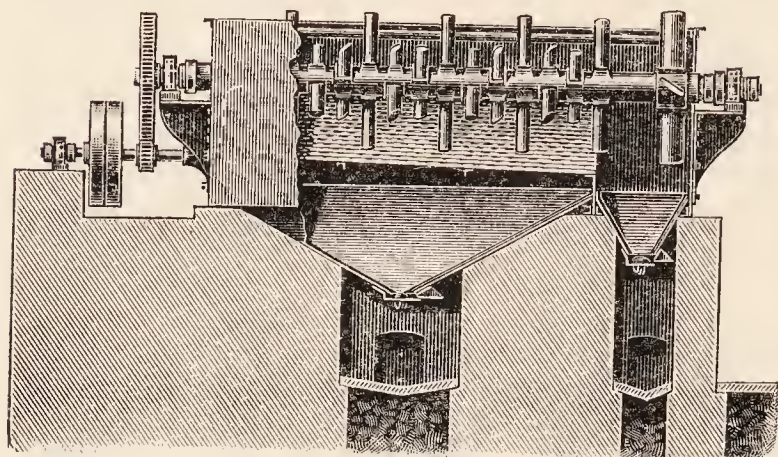


FIG. 3.

transported along an hydraulic carrier, provided with stone and sand catchers, to the factory building, and raised by means of a bucket elevator to the washers (Fig. 3) to be cleansed from all adhering stones and mud. After washing, the beets are lifted to an upper

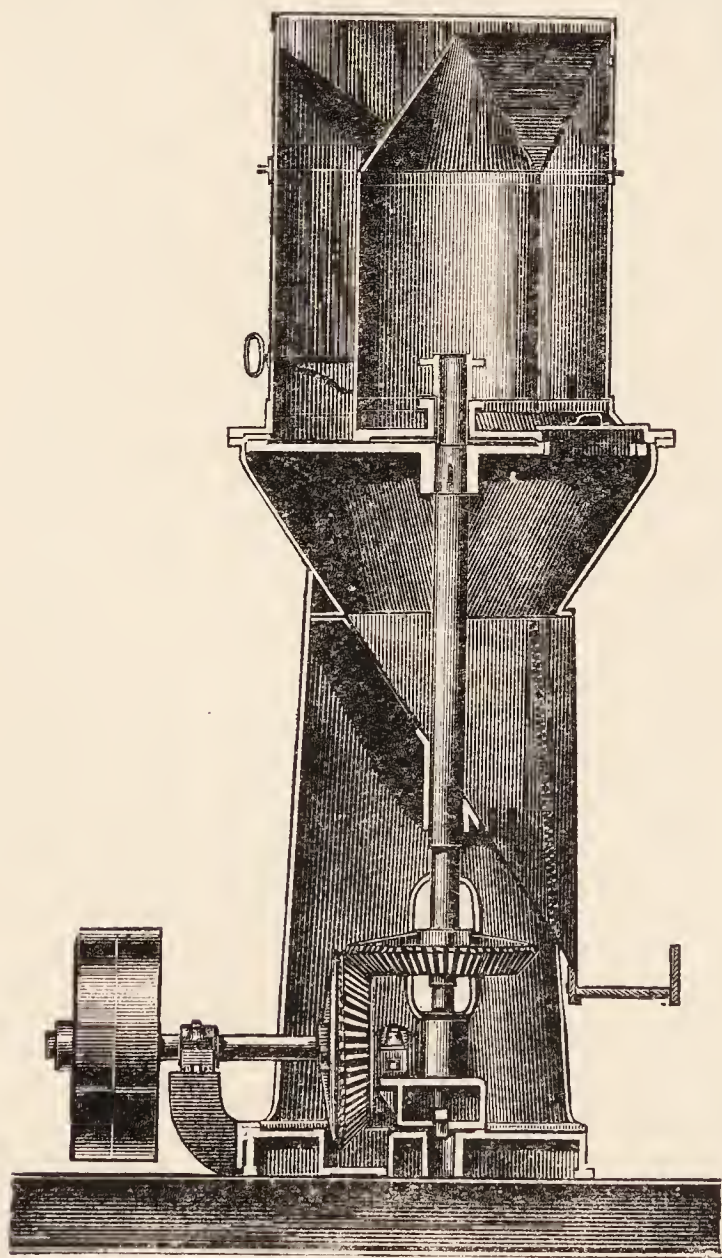


FIG. 4.

floor of the building, usually by a bucket elevator, to the weighing machine, which may be either an ordinary scale, or, preferably, may be of the more modern automatic type, taking about 10 cwts. in each weighing. From the hopper of the weighing machine, the beets are directed into the slicer (Fig. 4), to be there cut

up into fine, long shreds, technically known as 'cossettes,' 'slices,' or 'chips,' somewhat resembling vermicelli, in which form the extraction of the sugar is most readily effected by systematic lixiviation, or 'diffusion,' in a battery of 10 to 14 vessels termed 'diffusers.' In shape, diffusers vary somewhat, but the general and approved type is that of a vertical cylinder, with top and bottom in the form of truncated cones (Fig. 5). Both top and bottom openings are provided with securely fitting covers, the top one being opened usually by turning to one side, while the bottom one is generally counterpoised, and provided with an hydraulic joint. At the side of each diffuser is the 'calorizator,' which reheats the juice as it passes from one diffuser to another in the battery. The battery of diffusers is provided with suitable pipe connections, so

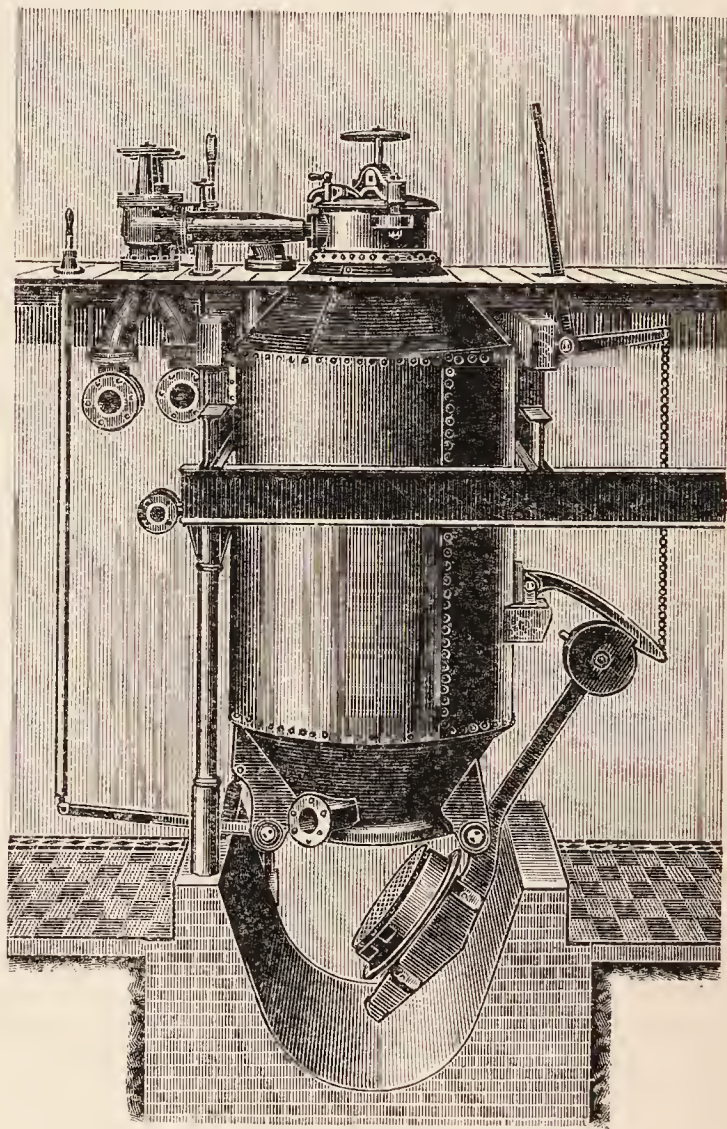


FIG. 5.

that either water may be admitted to each vessel, or the liquid contained in any vessel may be passed into its neighbour or drawn off when the operation is completed.

The cossettes or slices are conveyed from the slicers by a travelling band and directed by chutes into the top of the vessel to be filled, which is then securely closed. There still remains considerable interstitial space between the slices for liquids to be added.

When the battery first begins to operate, water at 87° to 90°C. is admitted to the first diffuser (No. 1) previously charged with cossettes, the water entering near the bottom and rising so as to displace all air. Dialysis now takes place through the walls of the minute vegetable cells of which the beet-cossettes are composed, the more crystallisable constituents of the beet-juice, such as sugar, diffusing into the surrounding water, whilst, simultaneously, water

diffuses into the interior of these cells. As the non-crystallisable impurities diffuse very slowly, or not at all, these remain behind in the cossettes after the sucrose has been completely extracted by repeated washings with water. After the first charge of water has been in contact with the cossettes in No. 1 diffuser for a few minutes, the resulting dilute solution is driven over into No. 2 diffuser by admitting fresh water into No. 1. Dialysis can now continue in No. 1 and simultaneously in No. 2. Similarly, a third addition of fresh water to No. 1 displaces the previously added water into No. 2, and that already in No. 2 into No. 3, thus causing further dialysis in Nos. 1, 2, and 3 simultaneously. These operations are repeated until the first charge of water entering No. 1 has passed through diffusers 2, 3, 4, and 5 into No. 6, and has extracted so much sugar that, if passed into No. 7, it could extract very little more. It is now termed 'diffusion juice,' and a measured quantity is drawn off from No. 6 into a measuring tank and is then treated in the factory. The previous operations are then continued, refilling No. 6 from No. 5, and No. 7 from No. 6. The maximum density is now obtained in No. 7, from which a measured volume is drawn off. No. 7 is then refilled from No. 6, and No. 8 from No. 7, and so on, until all the diffusers contain beet slices immersed in liquid of different densities.

The operations, so far described, represent the diffusion work *just beginning*. The *routine operations* then commence. The slices in No. 1, being practically free from sugar, are discharged by opening the bottom gate (Fig. 5). No. 1 is re-filled with fresh beet slices, and then becomes the last diffuser in the battery, instead of the first. No. 2 now becomes the first, No. 3 the second, and so on. Fresh water is next admitted to No. 2 (to extract the last portions of sugar), after which No. 2 is emptied and re-filled with fresh beet slices, thereby becoming the last diffuser in the battery, whilst No. 3 now becomes the first.

Thus, fresh water is passed into each diffuser in turn, and, simultaneously, strong diffusion juice is drawn off from other diffusers in turn. All the intermediate diffusers contain slices at various stages of extraction, and liquids varying in density from pure water to rich diffusion juice. The temperature to which the liquids are heated by the calorizators, when passing from one diffuser to the next, and the time these liquids remain in each diffuser, depends largely on the size of the diffusers, the quality of the roots treated, and the thickness of the slices.

When the diffusion juice leaves the battery it is cloudy, containing various matters in suspension, and is more or less dark in colour. It has a density of 14°–17°Brix, and contains 12–15 p.c. of sugar, as well as the greater part of the soluble constituents of the beet, such as the potassium and sodium salts of phosphoric, sulphuric, hydrochloric, oxalic, and tartaric acids, proteins, pectins, &c., and a small amount of invert sugar. In reaction it is slightly acid.

In order to separate the suspended fibre cellular tissue, and particles of pulp, the juice is passed through a pulp-separator, which consists simply of a vertical cylinder containing a perforated sheet-iron basket, and from thence passes through a juice-heater (Fig. 6).

This consists of a cylindrical steam drum, containing vertical tubes through which the juice flows continuously. The juice entering at A, passes upwards through one set of tubes, then downwards through another set of tubes, and, finally, upwards in order to reach the outlet B. Steam enters the drum at C through the valve B, the condensed steam draining off at D. By this means the juice is heated to 75°–80°, which has the effect of coagulating a portion of the albumen present, besides preparing for the following operation.

(2) *Chemical treatment of the juice.*—The object of chemical treatment is two-fold: (a) to clarify the juice, or render it transparent, and (b) to purify it by precipitating as much of

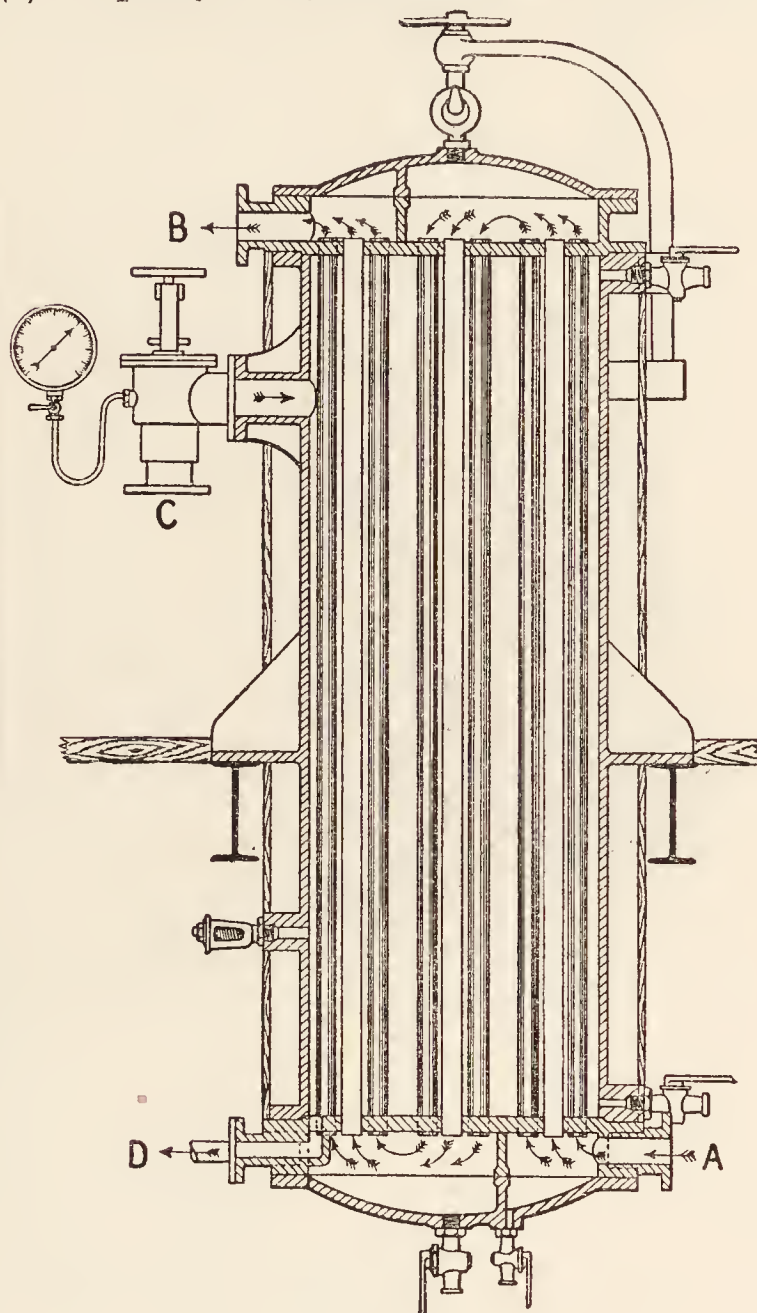


FIG. 6.

the dissolved impurities as possible. The chief chemical agent used for this purpose is caustic lime (calcium oxide), which is added to the juice either in the dry state or in the form of slaked lime (calcium hydroxide) mixed with water to the consistency of a cream, having a density of 20°Bé. Both methods yield equally satisfactory results, provided certain precautions are observed. The temperature should be at least 75°, and preferably 80°–85°, but not higher than 90°C., and the duration of contact between lime and juice should be from 5 to 10 minutes. In most factories, it is usual to add 2–3 p.c. of lime; and with this amount it is generally found that the juices are well defecated, light in colour, and filter readily, giving a good cake in the filter-presses.

The chemical action of lime *plus* heat on the constituents of the juice includes the following. The free acids and acid-salts present are neutralised; and insoluble lime salts formed with organic and inorganic acids, particularly oxalic and phosphoric acids, while potash, soda, and the organic bases present are liberated. Albumen is decomposed more or less completely, with the formation of albumoses, peptones, polypeptides, and amino acids; whilst the invert sugar is resolved into saccharic and lactic acids. In addition to this chemical effect, the resulting precipitate acts mechanically, since it entrains particles and filaments of the root suspended in the juice.

The juice, being now strongly alkaline, could not be boiled and concentrated to syrup without

becoming very dark in colour. Hence, the excess of lime added is first neutralised by means of carbon dioxide gas, forming calcium carbonate, which, being quite insoluble in the juice, can be separated by filtration. The treatment with the gas is termed 'carbonation' or 'saturation.' For this purpose, both the calcium oxide and carbon dioxide are simultaneously prepared by burning a mixture of limestone (calcium carbonate) and coke. This mixture is added at the top of a kiln, and gravitates slowly towards the bottom, during which it is heated to about 1000°C . and is decomposed, as shown by the equation: $\text{CaCO}_3 = \text{CaO} + \text{CO}_2$. The caustic lime is removed periodically from the base of the kiln, and the carbon dioxide gas from the top by

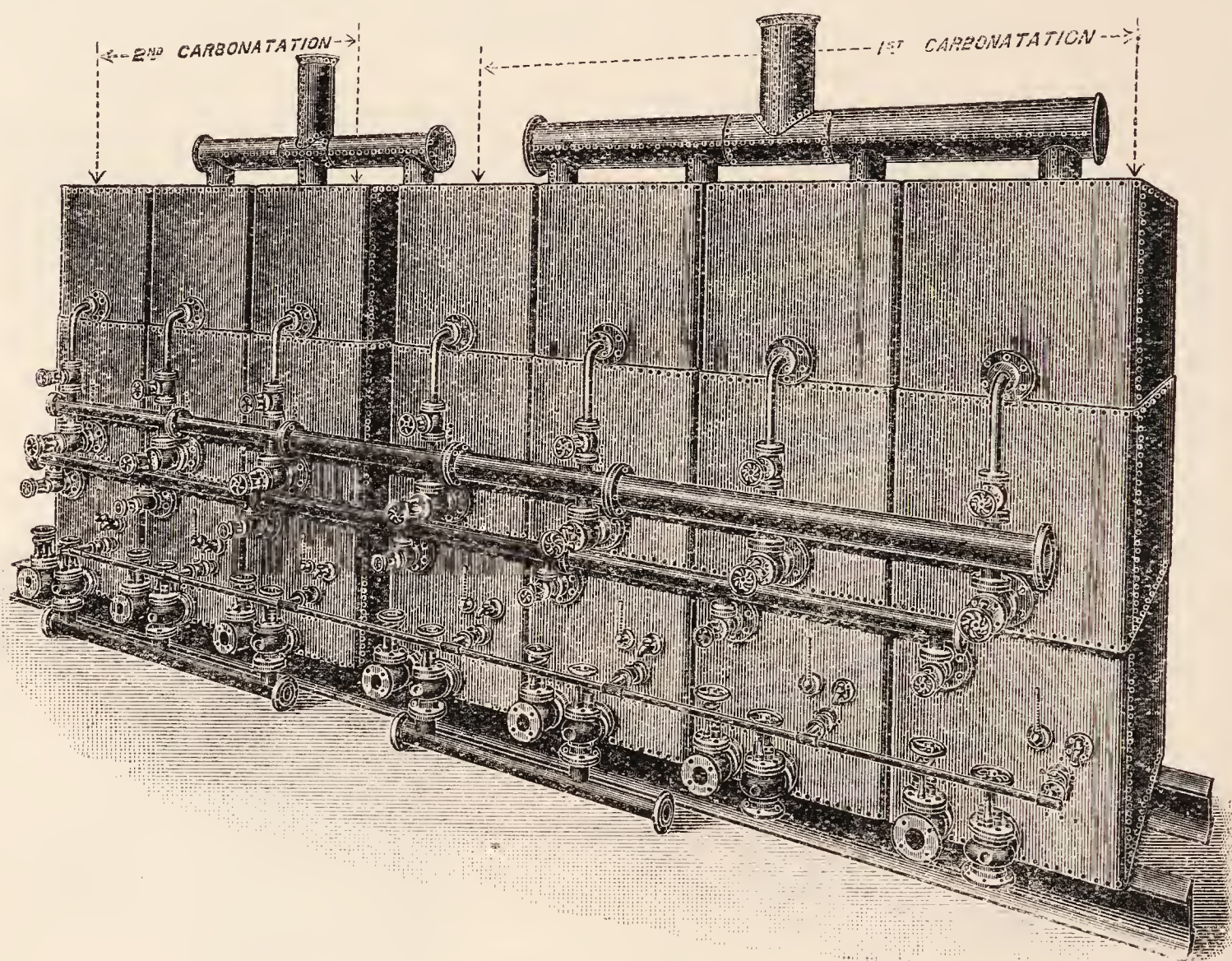


FIG. 7.

means of a pump, which forces the gas through pipes to the carbonation tanks.

These tanks may be circular or rectangular (Fig. 7), and are provided with steam coils for heating, and a gas distributing pipe causing the carbon dioxide to bubble through the juice during the operation.

On first passing the gas into the limed juice, a complex combination of calcium oxide, calcium succinate, and calcium carbonate, called 'sucro-carbonate of lime,' is formed which is very gelatinous. As the operation proceeds, this body gradually decomposes, with the formation of sugar and calcium carbonate. Saturation is continued until a sample shows that the precipitate, technically termed the 'scums,' is granular, and separates readily, leaving the supernatant liquid quite clear, the alkalinity on titration being about 0.1 p.c. calcium oxide,

using phenolphthalein as indicator. If more gas be added the precipitated impurities, including some of the colouring bodies, commence to re-dissolve.

The slightly alkaline juice is then passed through a filter-press (Fig. 8). This apparatus consists of numerous metal plates and open frames, arranged alternately, and separated from each other by layers of filter-cloth. The unfiltered juice passes into each frame and is thus confined between the two opposite filter-cloths. Filtered juice, passing through the cloths, flows down the corrugated surfaces of the plates on either side of the frame and escapes from small cocks shown in the illustration. The solid matters are held back by the filter-cloths until they completely fill the frames, thus forming cakes of the same thickness as the frames. These cakes consist chiefly of calcium

carbonate, together with the organic and mineral impurities which have been precipitated from the juice.

The clear, filtered juice is still slightly alkaline, but light in colour. It is once more

carbonated, in order to render it neutral. This second treatment may be carried out in the same type of apparatus as the first carbonation (Fig. 7), or in an apparatus through which the juice flows continuously. Generally both carbon

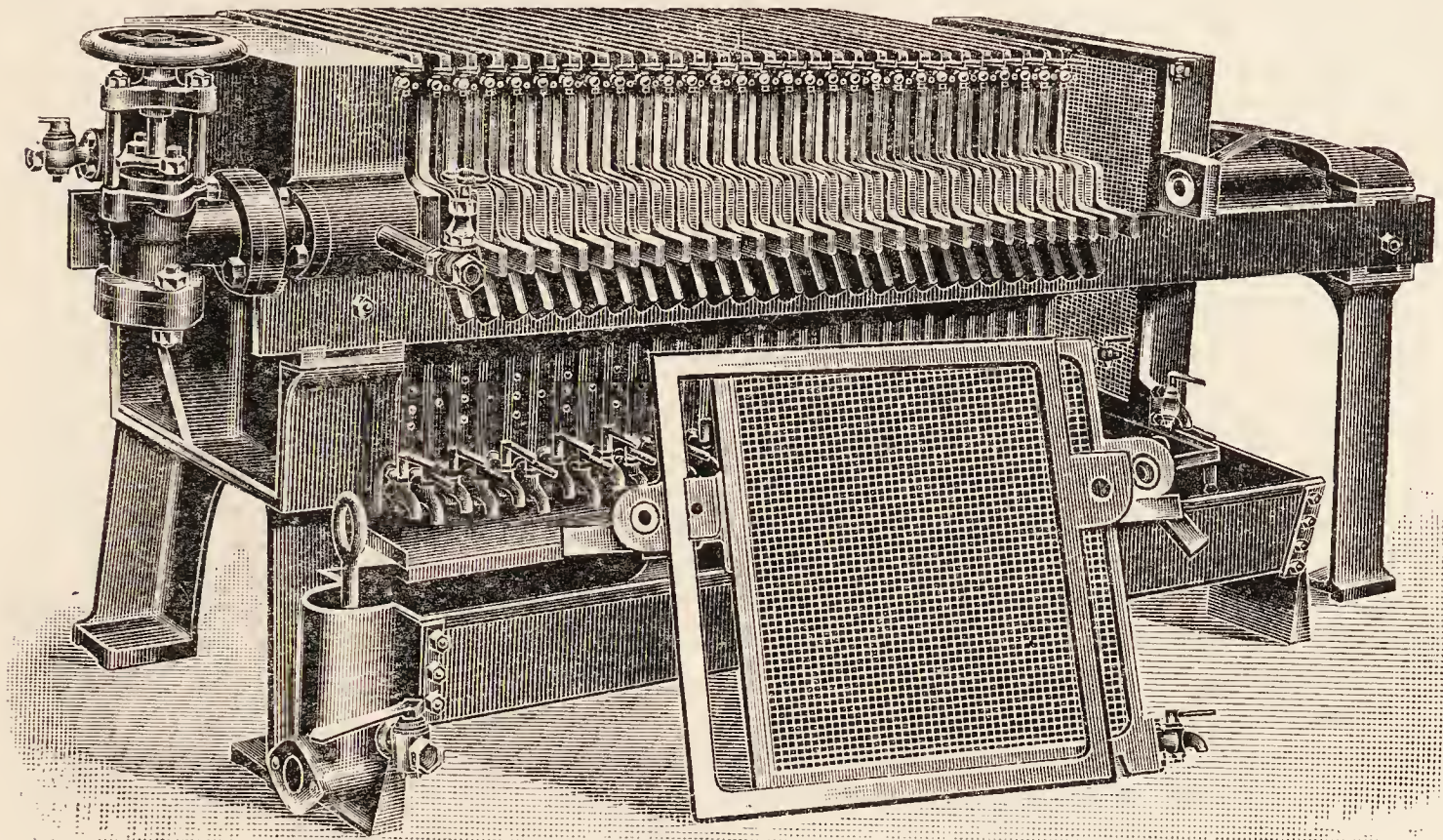


FIG. 8.

dioxide and sulphur dioxide are used, but if only carbon dioxide, a separate 'third saturation,' employing sulphur dioxide, follows, and in any case the final alkalinity is reduced to 0.01–0.04 p.c. calcium oxide. After each

saturation the juice is filtered through presses as before.

(3) *Concentration of the juice to syrup.*—In order that the contained sugar may crystallise most of the water present in the diffusion

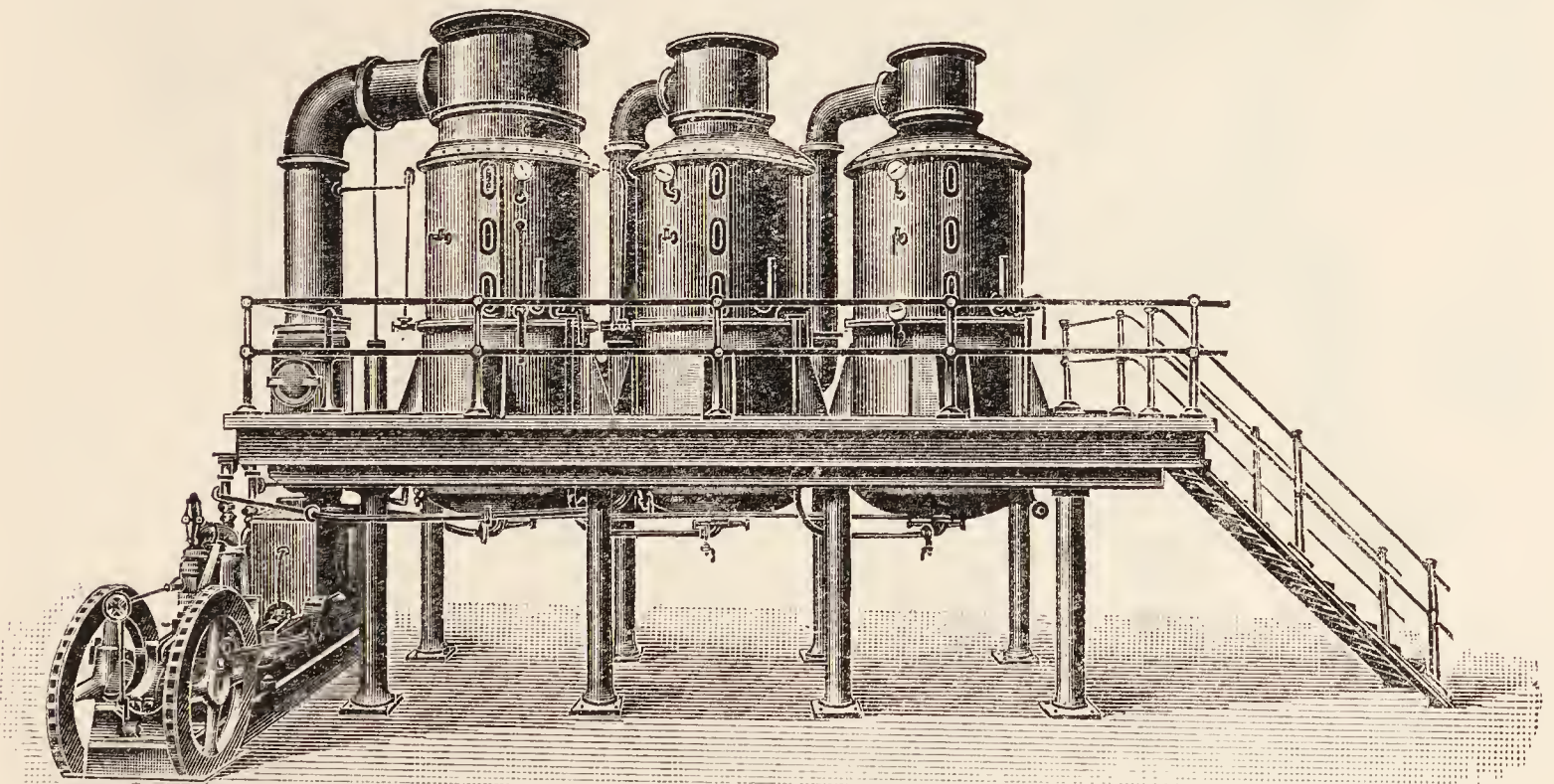


FIG. 9.

juice must be evaporated, and this is carried out in two stages. In the first, the dilute juice is concentrated to a thick syrup of 55°–60°Brix, by evaporating about 80 p.c. of the water. In the second stage, this syrup is further concentrated until crystals are formed,

and gradually increase in size by continued evaporation of water. Finally, a semi-solid material termed 'massecuite' is obtained, consisting of sugar crystals and a small amount of thick syrup. During both stages the juice or syrup is boiled *in vacuo*, thereby lowering the

boiling-point, and thus avoiding any decomposition of the dissolved sugar and organic impurities, which would cause the resulting sugar crystals to be dark in colour, and of lower market value.

The concentration of juice to syrup is carried out in the apparatus shown in Fig. 9, termed a 'triple-effect evaporator.' The three vessels are of exactly the same construction, the lower portion of each consisting of a steam drum with vertical tubes containing the juice. Steam is admitted to the drum in the first vessel (on the right) and transmits its latent heat through the metal walls of the tubes to the juice, which is thus caused to boil. The vapour escaping from the boiling juice enters a large pipe leading from the top or dome of vessel No. 1 to the steam-drum of No. 2. Here it is condensed, transmitting its latent heat to the juice present in No. 2, until this is also brought to the boiling-point (but at a lower temperature than in No. 1). Similarly, the vapour escaping from the boiling juice in No. 2 passes into the steam-drum of No. 3, causing the juice in the latter to boil (at a lower temperature than in No. 2). Finally, the vapour from the boiling juice in No. 3 passes to a condenser and air-pump (shown on the left). By this arrangement, 1 lb. of steam entering the steam-drum of No. 1 causes the evaporation of a nearly equal weight of water from the juice in No. 1, No. 2, and No. 3, or a

total evaporation of nearly 3 lbs. of water, hence the term 'triple-effect.' Four similar vessels

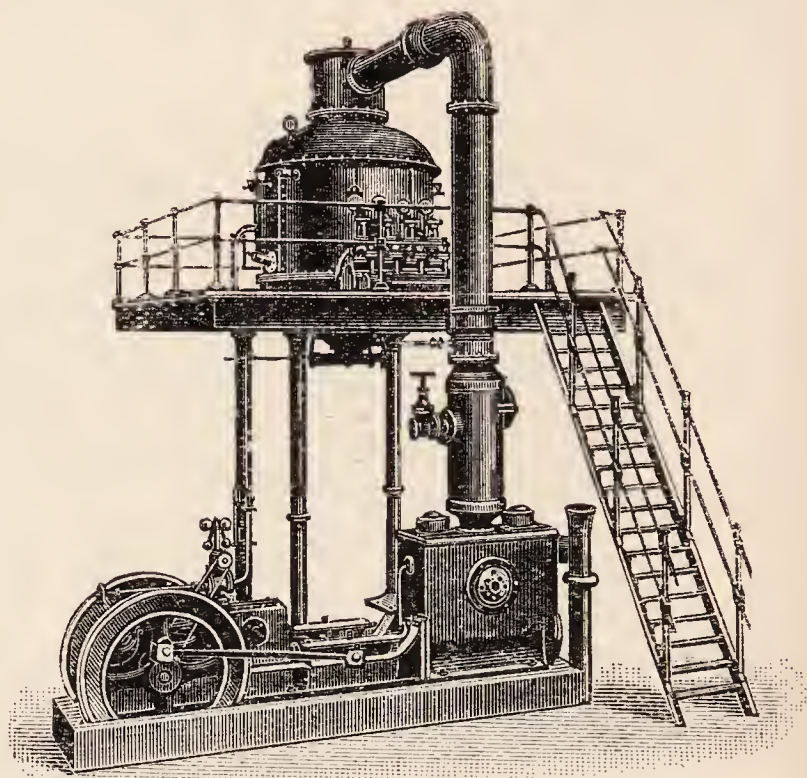


FIG. 10.

connected together form a 'quadruple-effect,' and five vessels a 'quintuple-effect,' enabling nearly 4 and 5 lbs. of water, respectively, to be evaporated

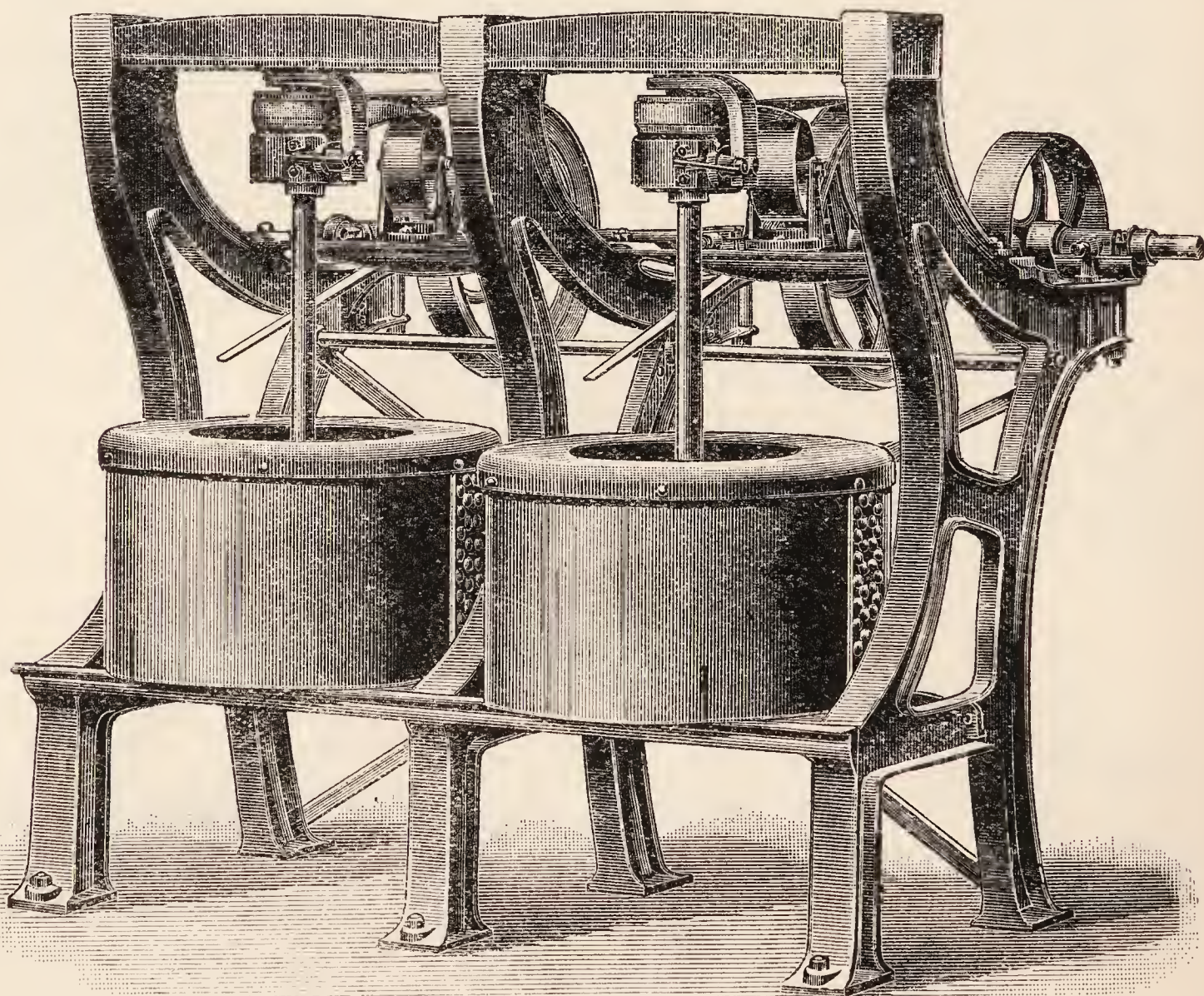


FIG. 11.

from the juice per pound of steam entering the first vessel. The high economy of the quadruple and quintuple effects is taken advantage of

in beet sugar factories in order to minimise the quantity of coal burnt in the furnaces.

(4) *Crystallisation of the sugar from the*

syrup.—The second stage of evaporation (referred to above) requires to be very carefully controlled, both as regards the degree of concentration and the temperature. This operation is, therefore, carried out in a separate apparatus called the 'vacuum pan,' shown in Fig. 10. This represents a 'single-effect' evaporator, the syrup being heated by means of several copper or brass coils, into which steam is admitted, the coils being arranged one above another, and each coil controlled by a separate steam valve. The capacity of the pans used may vary between 20 and 50 tons of sugar.

The object of the pan-boiler is to form a certain quantity of crystals or 'grain' in the thickened syrup, and then to allow the sugar passing out of solution during further boiling to deposit on these crystals, without the formation of new crystals, technically known as 'false grain,' which subsequently cause difficulty in the centrifugals. During the process of boiling, the pan-boiler is entirely guided by the appearance of the sample which he takes from the pan by means of the 'proof-stick' and from certain empirical tests, such as 'string proof.'

The crystals, when once formed, are caused to grow by frequently drawing fresh portions of syrup into the pan and evaporating the water therein. When the pan is full, the resulting 'massecuite' is finally concentrated until it contains from 5–10 p.c. of water, and is then discharged by opening the discharge-gate at the bottom. The pan is thus 'struck out' and the discharged contents are termed the 'strike.' This gravitates to large horizontal open troughs, called 'strike-mixers,' from which small charges can be drawn off into numerous centrifugal machines placed below the 'mixer.' Or the strike is discharged into large cylindrical horizontal vessels, called 'crystallisers,' fitted with stirrers, in which further crystallisation may take place during gradual cooling of the massecuite before it is treated in the centrifugal.

(5) *Separation of the crystals*.—The crystallised massecuite is a mixture of sugar crystals and mother-liquor; the former consisting of nearly pure sucrose, whilst the latter contains in solution all the organic and mineral impurities which the previous chemical treatment of the juice failed to eliminate. It only remains to separate the solid crystals from the impure mother-liquor (now termed 'green syrup') by means of a fine gauze strainer, which permits the fluid to pass through but retains the crystals. This is accomplished in centrifugal machines, two of which are shown in Fig. 11. This apparatus consists of an exterior stationary cylindrical casing (shown in the figure), and an interior drum or 'basket' (of smaller diameter than the casing) attached to the lower end of a vertical shaft or spindle. The spindle and basket are set in motion by a belt-driven pulley shown at the upper extremity of the spindle, and a large number of machines are driven off a single 'counter-shaft' (shown behind).

The basket is of steel, and of the same form as the exterior casing, but is perforated with numerous small holes. This perforated area is lined with fine copper gauze called 'the liner,' the apertures in which are of smaller diameter than the sugar crystals which are to be separated. The empty basket is set in motion, and a

charge of massecuite admitted through the central opening in the cover of the casing. The centrifugal force causes the massecuite to spread uniformly over the interior vertical liner, and drives the fluid mother-liquor through the mesh of the liner, thence through the perforated sides of the basket, into the exterior casing, from which it is discharged into a gutter, leaving the sugar crystals in the basket after the mother-liquor has escaped. The machine is then stopped, and the 'cured' crystals are discharged through a central opening in the bottom of the basket and corresponding opening in the casing. The diameter of the basket varies from 30 to

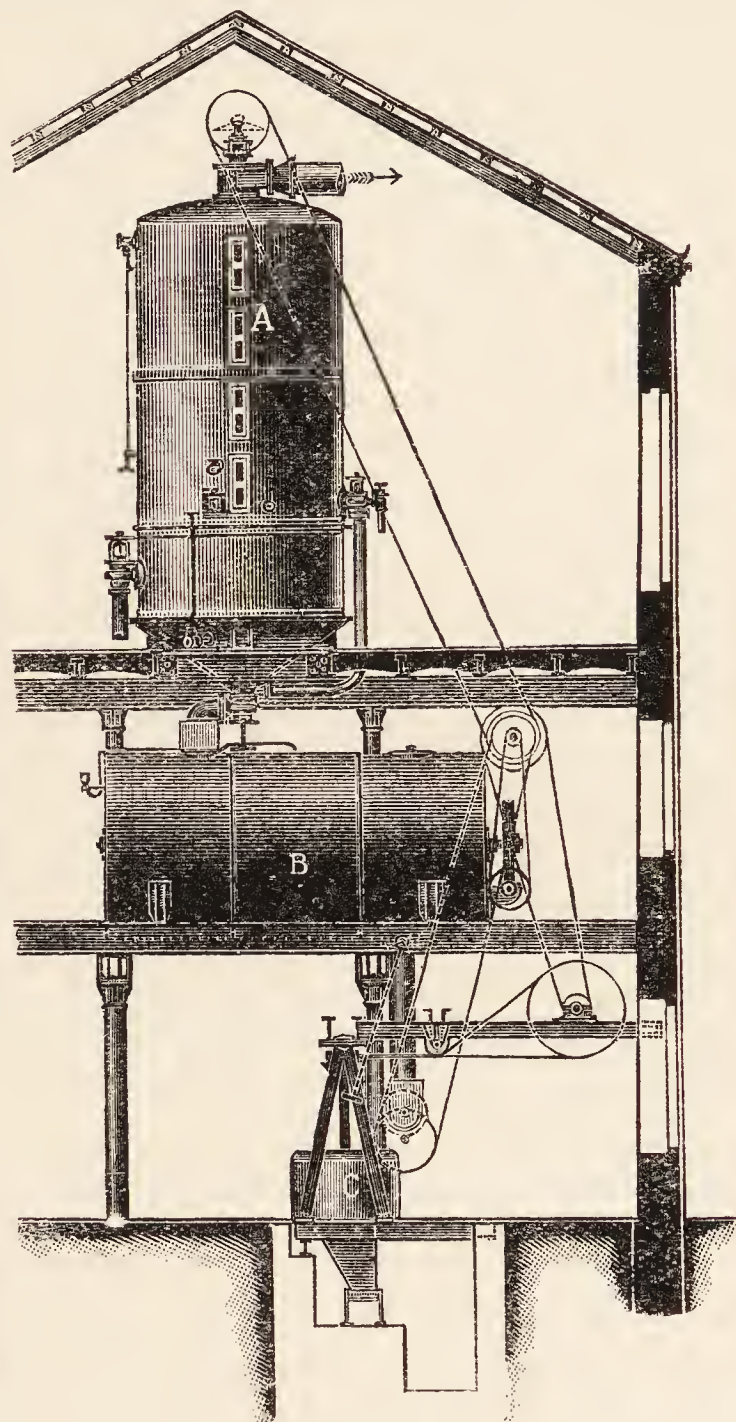


FIG. 12.

50 ins., and the speed of rotation varies from 800 to 1500 revolutions per minute. In Fig. 11, the counter-shaft is driven by belting from a steam engine. Other methods of driving include electric motor and water-turbine, both of which act directly on the centrifugal spindle.

It is convenient for the vacuum pans, crystallisers, and centrifugals to be on different floors, as shown in Fig. 12, so that the massecuite may gravitate from one to the other. Where this is not possible the massecuite may be transported and elevated (if necessary) by means of a special form of pump or by means of compressed air.

The mother-liquor, or 'green syrup,' also called 'centrifugal syrup,' escaping from the

centrifugals, undergoes the treatment described below under (6).

In making white (unrefined) sugar for direct consumption, the last traces of syrup are removed from the crystals as completely as possible, by washing with steam, water, or concentrated sugar liquor, while the machines are spinning, but in such a way that very little of the crystal is dissolved. A little ultra-marine is added to the water used for washing in order to conceal any residual yellow tint in the sugar.

White sugar obtained in this way may be sold as a cheap quality of 'granulated,' or may be ground to a form of 'powdered sugar.' or, again, the crystals may be converted by pressure into loaf sugar. Such products are not regarded as equal to refined sugars, although they find a ready market, especially on the Continent. They have not the brilliant whiteness of refined sugars, which can only be made by a further purifying treatment described below.

A more recent method of producing white sugar direct from the beet may here be mentioned. The beet-juice (diffusion juice) can be decolorised by treating it with certain carbons, such as 'Norit' (see article on DE-COLORISING CARBONS), or, after manufacturing white sugar by the carbonation process described above, the 'Norit' treatment may be applied to the 'green syrup' separated from the first grade sugar in the centrifugals. This decolorised syrup then yields white sugar in the place of inferior 'after-product' sugar.

The quality of raw beet sugar depends not only on the sucrose content, but upon other factors. The crystals should be well defined in shape and of uniform size and colour. Of more importance than the colour of the syrup adhering to the crystal is the colour of the crystal itself. If not white, a pale yellow is to be preferred to a grey, since a grey sugar is generally difficult to refine. Further, the raw sugar should have a sufficient alkalinity to phenolphthaleïn, otherwise it does not keep well on storage.

(6) *Treatment of the centrifugal syrup and the working-up of the after-products.*—The so-called 'green syrup,' has a purity of 70°–80°,¹ and contains an appreciable amount of crystallisable sugar, which is extracted in the form of a low-grade sugar termed 'after-product.'

It was formerly the custom to boil the centrifugal syrup in the vacuum pan to supersaturation with little or no formation of grain, and to allow the sugar crystals to separate in tanks, with or without the addition of inciting crystals or 'seed.' In using this method, it is necessary to repeat the boiling operation twice in order to exhaust the syrup to the purity of true molasses, and the second boiling must stand for some months before complete crystallisation is effected. Consequently, this method is expensive and inconvenient, the operations having to be continued after the campaign proper has terminated, although there is no doubt that the modifications introduced by Ehrhardt and Fölsche have been of much service in improving it.

¹ By the 'purity' or 'quotient of purity' is meant the percentage of sucrose in the total solid matter = $\frac{\text{sucrose} \times 100}{\text{total solids}}$.

In modern practice the centrifugal syrup is boiled to grain in the vacuum pan and the grain allowed to grow while being gradually cooled and agitated in a 'crystalliser.'

From the pan the massecuite is run into the crystalliser at a temperature of 85°–90°C., and gradually cooled to 25°–40°C. during 4 to 5 days, water being added from time to time in such amount that the supersaturation of the liquor is kept at the optimum for regular crystallisation (*vide* Herzfeld, *Zeitsch. Ver. deut. Zuckerind.* 1892, 174; and Claassen, *ibid.* 1897, 809). When crystallisation is completed the massecuite gravitates to the centrifugals to be separated into sugar crystals and mother-liquor.

On re-treating this mother-liquor in the same manner, a further separation of crystals is effected, the residual or final mother-liquor yielding no more crystals after further evaporation of water, followed by cooling. It is therefore termed 'exhausted or final molasses,' and has the following average composition: sucrose, 50 p.c.; non-sugars, including mineral matter, 30 p.c.; and water, 20 p.c. The purity is 58–60 p.c.

Brief mention may be made of modifications of the general method of treating after-products. In the Grossé process, boiling and crystallisation are both carried out in a special pan, fitted with a spiral agitator, in addition to the ordinary steam coils (A, Fig. 12).

In the Mathis method, the syrup is boiled to a high Brix content, filled into a special crystalliser at 95°–100°C., and there boiled under reduced pressure, graining being induced by the introduction of high-pressure steam or air. Karlik and Czapikowski have designed a horizontal graining pan in which the heating arrangement is in the form of a cross revolving about a hollow shaft at the rate of only 1–3 revolutions per minute.

Generally the after-product obtained by one or other of these methods is sold directly as low-grade sugar, but sometimes it is re-dissolved in the thin-juice, which is then worked up in the usual way. Re-solution in the thin-juice is also used in factories where a white (unrefined) direct consumption product is made.

In order to recover some of the sucrose in exhausted molasses, the latter was formerly treated by the 'osmose' process, by which a syrup of higher purity was obtained and re-boiled in the vacuum pan yielding an additional quantity of crystals. This has now been abandoned in favour of the Steffen or Schreiber processes, or modifications of them, in which an insoluble calcium or strontium saccharate is precipitated, separated by filtration through presses, and subsequently decomposed with carbon dioxide into sugar and calcium or strontium carbonate.

By-products of the beet sugar industry.—The leaves and 'tops' of the sugar beet are used as fodder for cattle, as are also the exhausted beet-slices called 'pulp,' discharged from the diffusion battery, after being pressed or partially dried. The cakes discharged from the filter presses consist chiefly of carbonate of lime, together with small percentages of organic and mineral matters separated from the juice, and are sold at a low price to the beet-growers to be applied to the land as a 'lime-dressing.' Lastly, the 'exhausted' or final molasses is utilised in one or

other of the following ways: (a) for the production of alcohol; (b) for mixing with other materials in the manufacture of 'molasses cattle-foods.' The well-known 'Molassine' is a meal prepared by absorbing the molasses in dried Iceland-moss. Molasses may also be blended with dried beet-pulp (see above), brewers' grains, peat, alfalfa meal, or other suitable absorbent; (c) for the manufacture of blacking, dyewood extracts, &c.; (d) as a manure, either alone or blended with other fertilisers, or the contained potash may be extracted and applied as a fertiliser.

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(b) MANUFACTURE OF RAW SUGAR FROM THE SUGAR CANE.

The manufacture of sugar from the cane differs from that of beet sugar only in the first two stages, namely: (1) *The extraction of the juice*, and (2) *The chemical treatment of the juice*; the subsequent operations (3) to (6) being practically the same as those already described under (a) 'Manufacture of raw sugar from the beet.'

(1) *Extraction of the juice.*—From very early times the sugar cane has been subjected to pressure between rollers, which ruptures the cellular structure of the stem, thus liberating the contained juice. The success of the diffusion process of extracting sugar from the beet naturally led to its application to the cane also, with the result that diffusion extracted much more sugar than the cane-mills formerly used, and led engineers to construct more powerful mills. The choice between milling and diffusion is influenced by other considerations, the most important of which relates to the supply of fuel for generating steam used in the factory. The sugar-cane stem contains from 10–16 p.c. of fibre, and the crushed cane leaving the mill contains from 35–50 p.c. of fibre. This crushed residue (called 'bagasse' or 'megass') can be burnt in special furnaces without further drying, and in a modern factory no other fuel is required. If the diffusion process be adopted,

the cane slices or 'chips,' when discharged from the diffusers, are saturated with water, and must be passed through a mill to render them suitable for fuel. Thus, diffusion must be *supplemented* by milling instead of being *substituted* for it, and the mill which is employed for extracting waste water could have extracted the juice direct.

This objection does not arise when diffusion is applied to the beet, as this material contains only 1–3 p.c. of fibre, and after extracting the sugar the residue or 'pulp' is quite unsuitable for fuel, even if dried. Coal must therefore be used as fuel and the 'pulp' is utilised as cattle-food, either in the wet state, or after partial drying.

Other disadvantages of cane-diffusion may be briefly mentioned. (1) Diffusion must operate continuously, day and night. This is possible when treating beet, because the roots can be stored in large quantities close to the factory. But when the sugar cane has been cut, it cannot be stored without deteriorating with consequent loss of sugar. (2) Cane being much harder than beet, the knives of the slicing machine are rapidly blunted and require frequent renewal. The slicing operation also consumes more power. (3) Diffusion requires experienced operators to carry on the work, whereas the mill is automatic in action after the mill-engine has been started. (4) The quantity of cane crushed per day can be varied by suitably adjusting the mill-rollers, whereas in the diffusion process the daily output is determined by the size or capacity of the diffusers.

These considerations sufficiently indicate why diffusion of cane has been abandoned in favour of milling, and is to-day only employed in one or two cane-sugar factories. The diffusion process has been previously described.

The Milling Process.

The earlier cane mills consisted of three horizontal iron rollers, about 6 ft. in length and 3 ft. in diameter. One roller is placed above the other two, causing the centres of the three rollers to form an isosceles triangle with horizontal base. The canes are elevated to a point above the mill by means of a travelling endless band, called the 'cane carrier,' which discharges them upon an inclined 'feed-plate' forming part of the mill. The canes are crushed twice, first between the 'top' and the 'front' (or 'feed') rollers, and again between the 'top' and the 'back' (or 'bagasse') rollers. This arrangement is, therefore, equivalent to two separate pairs of rollers, but is much more compact. After the first squeeze the crushed cane passes between the 'top' roller and a rigid curved steel plate, called the 'trash plate' or 'trash turner,' the motion of the 'top roller' moving the material across this plate until it can be gripped between the 'top' and 'back' rollers. After this second squeeze the crushed fibre emerges above the 'back' roller and gravitates down an inclined 'discharge plate' at the rear of the mill. The extracted juice flows over the surfaces of the two lower rollers and falls into a receiver below, from which it gravitates to a pump. The motive power is usually steam, the rotary motion of the engine-shaft being transmitted, but at a much lower speed, to the projecting shaft of the 'top roller'

by means of compound gearing, and from the 'top roller' to each of the lower rollers by means of pinions. This 3-roller mill has been termed a 'single-crushing' plant, because forming a single unit. It is only capable of extracting from 60 to 70 p.c. of the total sugar in the cane, but was largely employed about thirty years ago.

The modern mill consists of several 3-roller mills or units combined, thus forming a 'multiple crushing' plant. Fig. 13 shows a combination of four 3-roller mills (with the addition of two special rollers placed in front) or a 14-roller mill, subjecting the cane to nine successive squeezes. The crushed fibre is conveyed from each mill-unit to the next by means of short 'intermediate carriers' similar to that which elevates the cane to the 'feed-plate' of the first mill-unit. From the last mill (shown in the foreground of Fig. 13) another 'carrier' or 'transporter' conveys the bagasse to the furnaces.

The two special rollers in front of the first mill are designed to cut the entering canes into

short pieces, and for this purpose their surfaces are deeply corrugated with zig-zag grooves, the projections on one roller interlocking with those on the other. This apparatus is termed a 'crusher,' but its true function is rather to prepare the cane for crushing in the mill itself. The 'Krajewski crusher' is the best known type. Another apparatus for the same purpose, termed a 'shredder,' tears up the cane into thin shreds, but without extracting any juice.

An important feature of the 'multiple mill' is that the crushed cane can be saturated with hot or cold water during its passage from any one mill-unit to the next, hence the terms 'saturation,' 'maceration,' 'imbibition,' and 'wet-crushing.' The 3-roller mill, when used alone, can only extract juice by pressure, and is said to perform 'dry-crushing.' In 'wet-crushing' the added water mixes with and dilutes the small quantity of unextracted juice present in the bagasse, causing the following mill to extract a large volume of diluted juice.

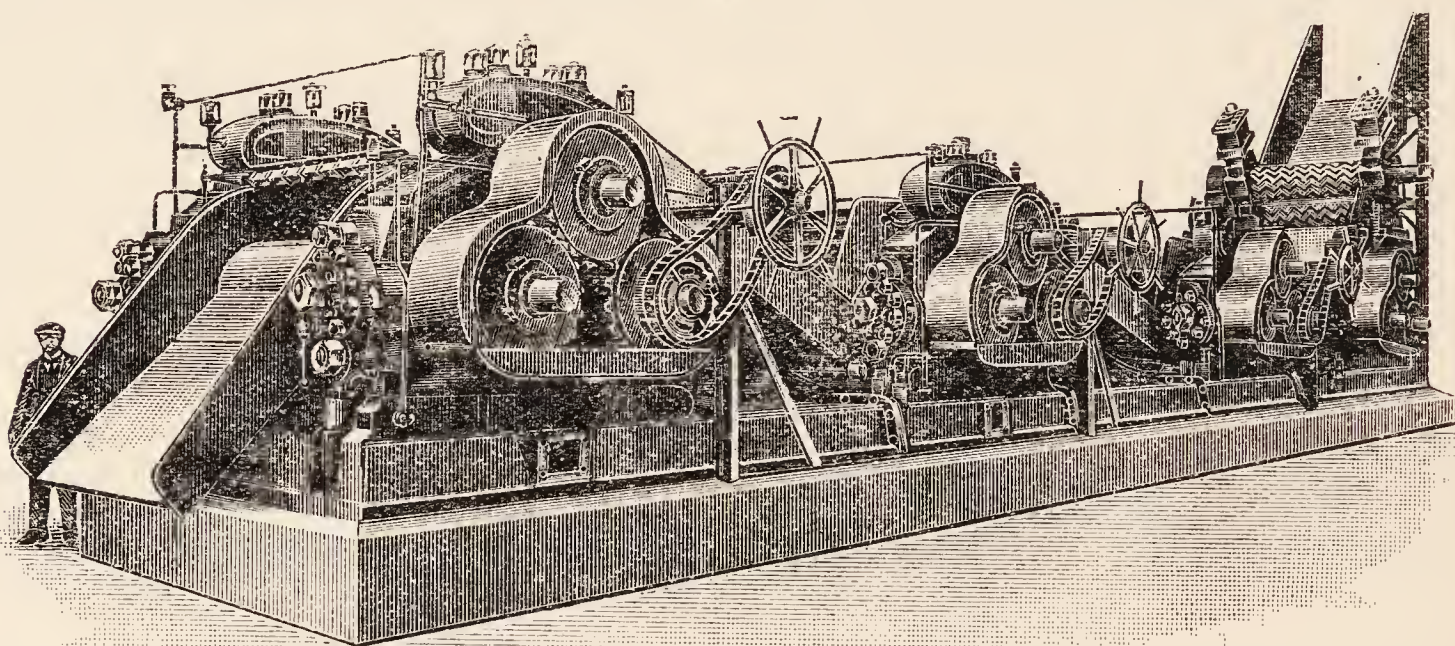


FIG. 13.

When the mill-units are arranged close together (as in Fig. 13) water is sprayed upon the bagasse from perforated water pipes. When the mill-units can be placed farther apart the bagasse can be immersed in water contained in a long shallow bath whilst passing from mill to mill. The former method is more generally adopted, because it permits 2 or 3 mill-units to be driven by a single engine. To avoid excessive dilution of the extracted juice (and subsequent evaporation of water) the most dilute juice, extracted by the last mill-unit, may be sprayed upon the bagasse leaving an earlier mill-unit, a mode of working called 'compound saturation.' Thus, in Fig. 13, pure water would be sprayed upon the bagasse leaving the third mill, and the dilute juice extracted by the fourth mill would be sprayed upon the bagasse leaving the second mill. Again, the partially diluted juice extracted by the third mill would be sprayed upon the bagasse leaving the first mill. The first mill and Krajewski crusher would thus extract undiluted juice (by pressure alone); the second mill would extract slightly diluted juice; and the more diluted juices extracted by the third and fourth mills would be employed for saturation, in addition to the pure water applied between the third and fourth mills.

Three recent improvements in the milling process must be mentioned. (1) The 'Searby shredder,' which, as explained above, prepares the cane for the heavy pressure in the mill. (2) The 'Meschaert grooving' of mill rollers, which provides a free outlet for the extracted juice when the canes or bagasse pass between the rollers, thereby increasing the extraction by preventing the absorption of juice by the bagasse in contact with it. (3) Other forms of grooving, to prevent 'slip' and increase the quantity of cane crushed per hour.

The efficiency of the mill-work is usually expressed as the percentage of sugar in the form of extracted juice on the total sugar in the canes crushed, and depends on the number of mill-units employed, and the quantity of saturation water that can be profitably applied. Thus, with 3-rollers (dry crushing) the extraction is about 70 p.c.; with 6-rollers (dry-crushing) 83-85 p.c.; with 8-rollers (or 2 units and crusher) and added water 10 p.c. on weight of cane, extraction 88 p.c.; with 11-rollers (or 3 units and crusher) and added water 20 p.c. on cane, extraction 92 p.c.; with 14-rollers (or 4 units and crusher, as in Fig. 13) and added water 20 p.c. on cane, extraction 94 p.c., and with 25 p.c. water, from 95-96 p.c.; with 20-

rollers (or 6 units and crusher) and added water 30 p.c. on cane, extraction 98 p.c. This last result is largely due to the recent improvements referred to above, and is equal to the best extraction by diffusion.

Instead of increasing the number of mill-units, attempts have been made to wash the unextracted juice out of the bagasse after the canes have been crushed in one or two mill-units. In the '*Perichon system*' the bagasse is washed in specially designed waggons, with perforated bottoms, the same portion of water being added to several waggon loads of bagasse, until it attains a suitable density. In the '*Geerligs-Hamacker system*' the bagasse is washed in vessels exactly resembling a diffusion battery, and operated in the same manner as for diffusion. In the '*Hinton-Naudet process*' diffusion vessels are employed for filtering the rich juice extracted by the mill (after the juice has been limed and heated) through the bagasse, also obtained from the mill, and, subsequently, for washing the remaining juice out of the bagasse by operating the battery in the same manner as for diffusion. Such methods may extract a little more sugar from the cane, but, owing to the increased extraction of impurities, it is doubtful whether the additional sugar can be caused to crystallise from the extracted juice.

(2) *Chemical treatment of the juice.*—The raw juice leaving the mill is an opaque, dark green liquid, which cannot be filtered until it has undergone some chemical treatment. It contains from 13–18 p.c. of sucrose; 0.5–1.0 p.c. of reducing sugars (chiefly glucose); 0.25–0.70 p.c. of mineral matter; and 0.2–0.5 p.c. of organic non-sugars, including nitrogen compounds, organic acids, colouring matters, pectin, and gums. The purifying agent is lime (as in the case of beet juice) combined with heat, but the quantity of lime added and the use of other chemical agents depend on the class of sugar to be made, namely (a) raw sugar for refining; (b) yellow crystals or 'Demerara sugar' for direct consumption; and (c) white crystals for direct consumption.

(a) In making raw sugar for refining, only sufficient lime-milk is added to neutralise the natural acidity of the juice, or to render the juice faintly alkaline. The limed juice is then heated to boiling-point by passing through one or more juice-heaters (Fig. 6), and passes into numerous settling tanks, called 'clarifiers,' which are filled in rotation, and the impurities allowed to subside for about 1 hour. Or the juice may be pumped direct from the mill through the juice-heaters and the lime-milk subsequently added to the hot juice in the subsiding or clarifying tanks. Both methods produce a flocculent precipitate of organic and mineral impurities, which slowly subsides, forming a sediment, leaving the bulk of the juice transparent and of a greenish-yellow colour. This clear juice is drawn off and passes to the multiple-effect evaporator (Fig. 9). The sediment, which still contains much juice, is pumped through filter-presses (Fig. 8) and the resulting filtered juice also passes to the multiple-effect evaporator.

(b) In making 'yellow crystals' for direct consumption, the raw juice is first bleached by the action of sulphur dioxide gas, produced by

burning roll-sulphur in a small furnace (see A, Fig. 14) through which a current of dry air is drawn by means of a steam-ejector (c), which also forces the sulphur dioxide fumes into the wooden chamber or 'sulphur box' (JJ). The

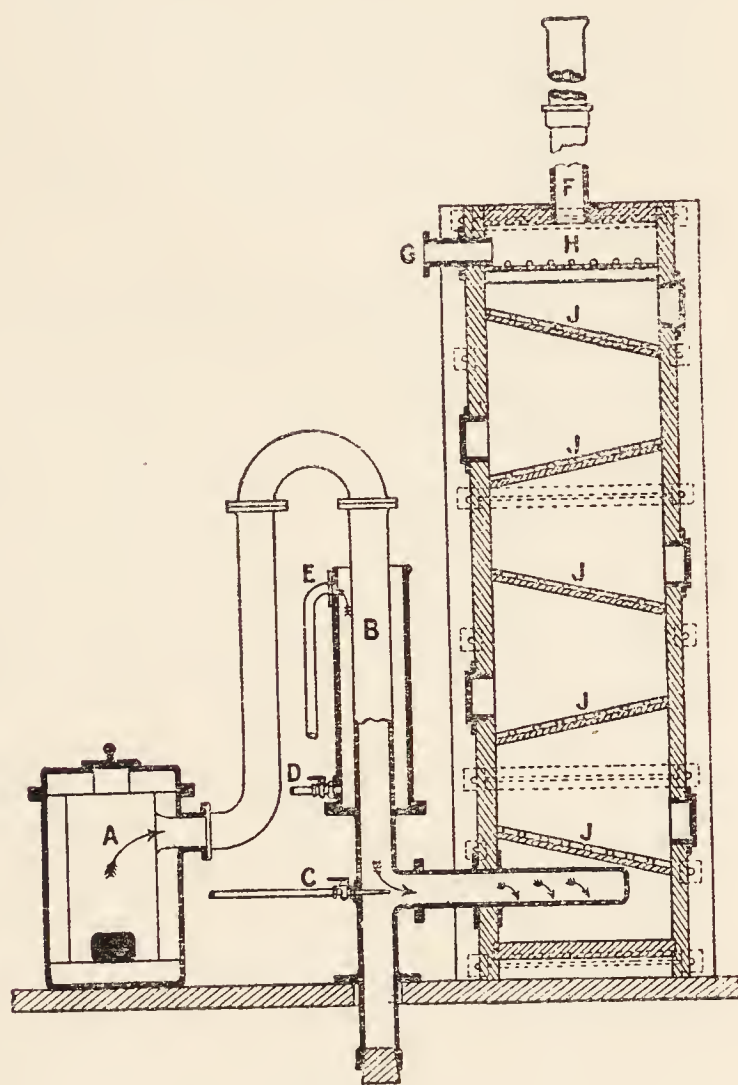


FIG. 14.

cold juice is pumped into the top of the chamber at (G) and descends in the form of a shower from the numerous perforated trays (JJ), finally escaping from an outlet at bottom. Any excess of gas escapes through the chimney (F), but the

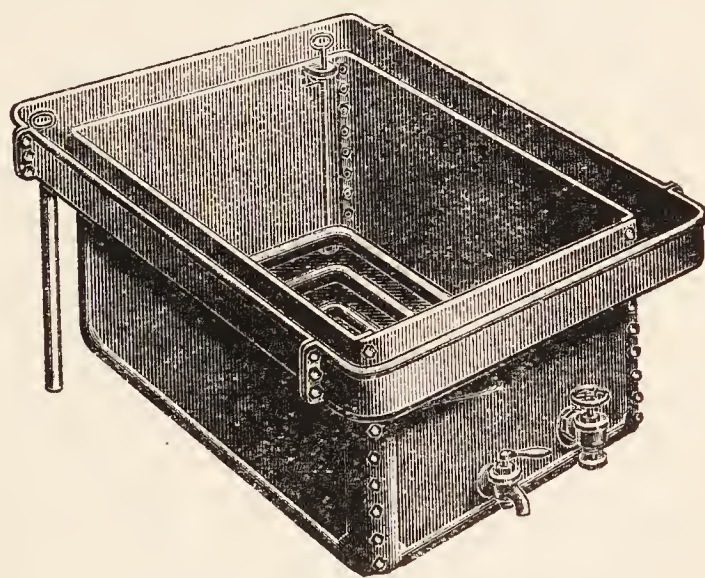


FIG. 15.

gas should be completely absorbed by the descending shower of juice. The bleached juice is then pumped through juice-heaters (Fig. 6), passing thence to the subsiding tanks or 'clarifiers,' where it is limed until only faintly acid. After subsidence the clear juice should have a pale straw colour. It next gravitates to special tanks called 'eliminators' (Fig. 15), fitted with steam coils at bottom, where phosphoric acid

is added, the juice vigorously boiled, and the foam brushed into the gutter which surrounds the top of the vessel. This treatment separates some of the previously added lime in the form of insoluble calcium phosphate, and also separates any particles of suspended impurities which the previous subsidence had failed to remove. The clear juice then passes to the multiple-effect evaporator (Fig. 9) to be concentrated to syrup. The sediments in the subsiding tanks and the scums separated in the eliminators are filter-pressed, and the filtered juice also sent to the evaporator.

The fine yellow colour of the sugar crystals is derived from the natural colouring matter of the cane, modified by the chemical treatment of the juice, described above, and further modified by the addition of stannous chloride to the crystalline massecuite whilst boiling in the vacuum pan (Fig. 10). No colouring matter is added at any stage of the manufacture. An imitation 'Demerara sugar' is produced by adding aniline dye to the boiling syrup in the vacuum pan, or, more usually, to the sugar crystals in the centrifugal machine after the molasses have been separated.

(c) In making white crystals two entirely different methods are used. (1) In the *carbonation process* (previously described under (a) *Manufacture of raw sugar from the beet*) a light-coloured juice and syrup is obtained without employing any bleaching agent. The most recent development in the manufacture of white sugar direct from cane juice is the 'Batelle process,' the essential feature of which consists in completely destroying the reducing sugars present in the raw juice by boiling the latter with from $1\frac{1}{2}$ to $3\frac{1}{2}$ p.c. of lime, after which the juice closely resembles beet juice and is treated by the carbonation process in exactly the same manner as beet juice. This treatment also permits the sucrose left in the final molasses to be extracted in the form of lime saccharate by the well known 'Steffen process' used in the beet-sugar factory, but hitherto inapplicable to cane molasses. The lime used for decomposing the reducing sugars is also utilised for extracting the sucrose from the final molasses.

(2) In the *Sulphitation process*, the bleaching action of sulphur dioxide and its compounds are utilised in much the same manner as in the manufacture of yellow crystals. In both methods the whiteness of the finished sugar is largely due to washing the crystals in the centrifugals after the coloured molasses have been separated, for which purpose either water or strong syrup may be used. A much better result is obtained by discharging the sugar (freed from molasses) into a mixer, where it can be thoroughly blended with the 'washing-syrup' and then again treated in centrifugals, to separate the 'washing-syrup.' This mode of working is termed 'double curing.' Should the final crystals still show a faint yellow tint, this may be concealed by adding an emulsion of ultramarine or aniline-blue whilst the centrifugal is running. Sufficient blue is thus distributed between the separate crystals to neutralise the pale yellow tint which washing fails to remove. This operation is called 'blueing the sugar.'

The bleaching of the raw juice with sulphur dioxide gas is frequently supplemented by a

further bleaching of the syrup during boiling in the vacuum pan, by adding 'Blankit' (sodium hydrosulphite) or 'Rédo' (calcium hydrosulphite), both of which exert a reducing action on the colouring matters present. Experiments have also been made with the decolorising carbon 'Norit' as a substitute for sulphur dioxide and its compounds, as previously described under the manufacture of white sugar from the beet.

For the removal of gummy, oily, and waxy matters from raw cane sugar, see Keyworth and Forster (J. Soc. Chem. Ind. 1924, 43, 203 T).

By-products of the cane-sugar industry.—The green leaves of the cane, also the uppermost joints or 'tops' of the stem, are utilised as fodder if not required for planting material (see description of the sugar cane). Reference has been made to the fuel value of the crushed cane, or 'bagasse,' and this by-product has also been successfully used for paper manufacture, which might be combined with sugar manufacture in localities where some other cheap form of fuel is abundant, to serve as a substitute for bagasse. The filter-press cakes, which contain a good deal of fibre, also nitrogen, phosphates, and organic matters, are generally employed as fertilisers on the cane fields. These cakes also contain canewax, which can be extracted by means of benzene and the solvent recovered by distillation for use over again. The extraction of this wax has developed considerably in Natal, because the 'Uba' cane there cultivated is richer in wax than most other cane varieties. After extracting the wax the residual press-cake can still be utilised as a fertiliser. The final or 'waste molasses' of the cane-sugar factory is usually converted into alcohol by fermentation, followed by distillation. It may also be converted into a useful cattle food, 'Molascuit,' by absorbing the hot molasses in dried bagasse dust, forming a moist meal. In many factories molasses is used as fuel to supplement the bagasse, being sprayed upon the bagasse before the latter enters the furnaces, or it may be burnt separately in special furnaces, and the potash subsequently extracted from the ashes. Cane molasses is also utilised as a fertiliser, either in the liquid form or mixed with other fertilisers. A substitute for petrol is manufactured in Natal under the name of 'Natalite,' by fermenting the molasses, distilling off the resulting alcohol, and treating the alcohol with sulphuric acid so as to produce a mixture of alcohol and ether.

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Journals.—The International Sugar Journal,

London; The Louisiana Planter, New Orleans; Revista Industrial, Tucuman; Australian Sugar Journal, Brisbane; American Sugar Industry and Beet Sugar Gazette, Chicago; Archief voor de Suikerindustrie in Nederlandsch-Indië, Soerabaia, Java.

(c) SUGAR REFINING.

As stated above, white sugar can be made direct from the cane and beet, but a purer and whiter product is obtained by first converting the impure plant-juice into crystals of moderate purity, and subsequently dissolving this raw sugar in water, decolorising the resulting solution, and recrystallising. The second stage is usually carried out in a separate factory, called the refinery. Refined sugar is made from raw cane and beet sugars, or from a mixture of both, and includes the following varieties:—

Dry Sugar:

(a) 'Granulated' = detached crystals of medium size.

(b) 'Crystal sugar' = detached crystals of large size, called 'Coffee sugar' in England.

(c) 'Castor sugar' = detached crystals of smallest size.

(d) 'Loaf sugar' = small crystals adhering together in blocks of conical form.

(e) 'Cube sugar' = small crystals adhering together in small cubes.

(f) 'Icing sugar' = any one of the above ground to a state of fine powder.

Moist Sugar:

(g) 'Yellow crystals' = white granulated coloured by the addition of a dye in imitation of 'Demerara sugar' made direct from sugar cane, as described above.

(h) 'Soft pieces' = a lower grade refined sugar consisting of very small crystals, admixed with sufficient treacle to render the mixture moist and yellow in colour. It is of lower purity than the raw sugar entering the refinery.

As all the above varieties are produced only in the later stages of refining, the main operations of the refinery must first be described, and are as follows: (1) preliminary washing in centrifugals; (2) melting; (3) filtration; (4) decolorising; (5) boiling to grain; and (6) separation of the crystals in centrifugals, or in moulds; (7) drying.

(1) *Preliminary washing treatment in centrifugals.*—Raw sugar, as previously pointed out, consists of crystals and adhering molasses, so that by washing off the latter the purity of the sugar is considerably raised and the process of refining facilitated. This preliminary washing, called 'affining,' is effected by mixing the sugar with syrup, to render it sufficiently liquid, and running it into a centrifugal machine (Fig. 11), either of ordinary or of special construction, the speed of which is generally 800 to 900 revolutions per minute. Steam, water, or sugar solution is admitted into the interior of the basket, but discontinued as soon as the outflowing syrup is light coloured, the machine then being stopped as quickly as possible.

The time required for the operation varies from 10 to 40 minutes, according to the quality of the raw sugar treated. For steaming, exhaust steam from the engine driving the machines is sufficient. Its pressure should not

exceed 5 lbs. in the pipes leading to the machines, and it should be dry.

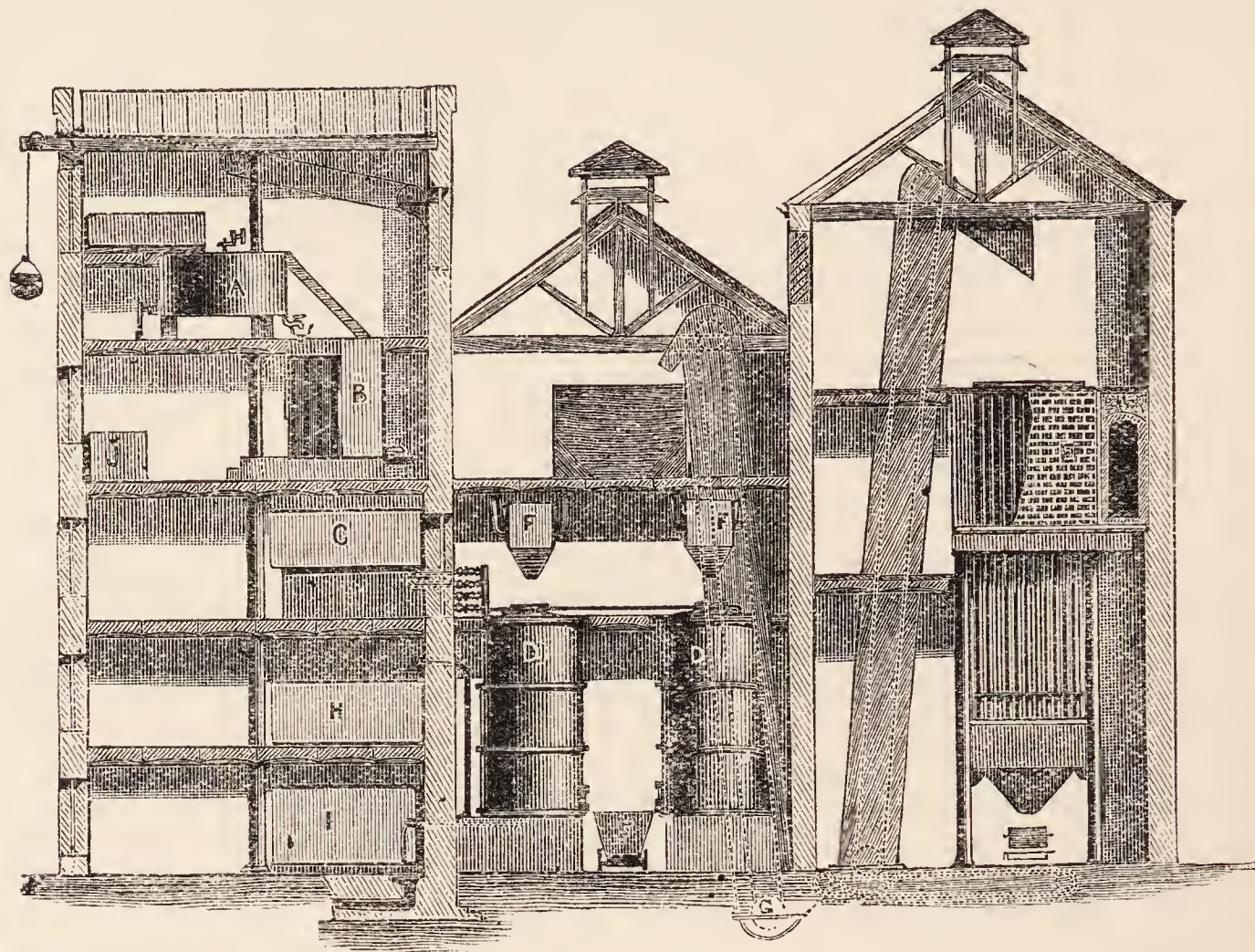
With large-grained raw sugar the yield of affined product may be from 80–90 p.c., but with low grade sugars it is usually only 65–70 p.c., the balance of the sugar remaining in the syrup. The affined sugar, if made from a large-grained raw sugar, will contain from 99–99.5 p.c. of sucrose, but if from a raw sugar of lower quality, only 97.5–98.5 p.c.

(2) *Melting or Dissolving.*—After the preliminary washing the sugar is elevated to the 'blow-up' or melting pans, which are generally situated on an upper floor of the refinery (Fig. 16). These blow-ups are cylindrical in shape, and are made of cast iron. Each is capable of holding from 3 to 10 tons of sugar, and the water sufficient to dissolve it; it is provided with a stirring gear and a copper coil, which is heated by low-pressure steam, or the coil is perforated with holes so as to blow in open steam. Thus by means of hot water and steam the sugar is rapidly dissolved, and by the addition of more sugar or water, as required, the solution is brought to the required density and temperature, viz. about 28°Bé. and 160°F.

(3) *Filtration.*—The 'liquor' or syrup obtained in the 'melting-pan' is an opaque, dark brown liquid, containing many suspended impurities which are removed by filtration through cloth. The apparatus generally used for this purpose is the 'Taylor bag-filter,' shown partly in section in Fig. 17. The upper portion forms a shallow tank from 6 ins. to 1 ft. in depth, into which the unfiltered syrup is pumped. From numerous holes in the bottom of this tank the syrup gravitates into long cloth bags suspended from the tank by means of nozzles, and the bags are surrounded by a cast-iron casing into which steam is led, so as to heat the bags and facilitate filtration. The filtered liquid flows over the exterior surfaces of the bags and falls to the floor of the chamber, where it escapes through an outlet pipe, and the solid impurities remain inside the bags in the form of a moist 'sludge.' The bags can be removed for cleaning and be replaced by clean bags by opening small doors in the outer casing.

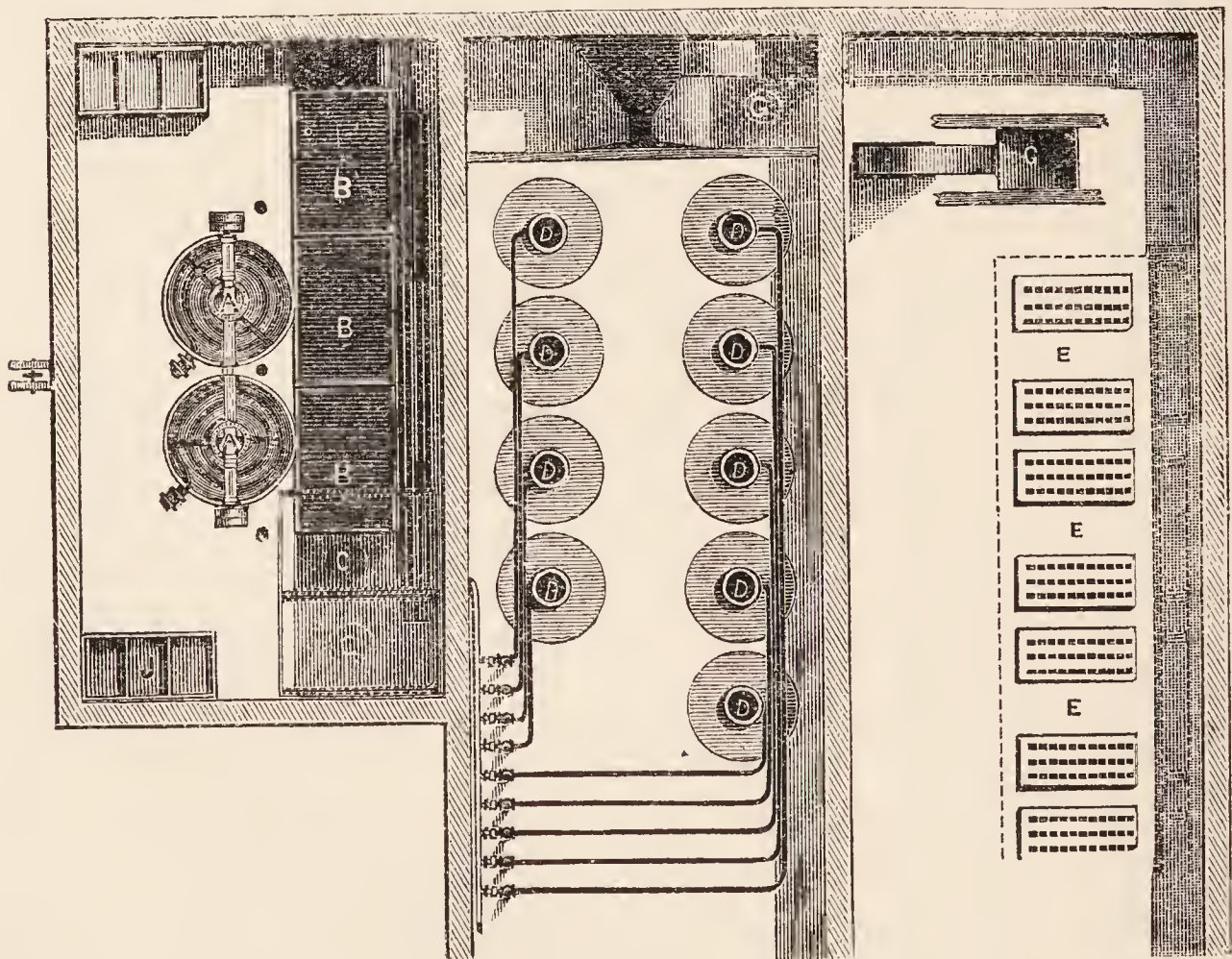
(4) *Decolorisation.*—The filtered liquor is next brought into contact with bone-char (see article on DECOLORISING CARBONS) in large cylindrical vessels called 'char cisterns,' or 'char filters,' usually about 18 ft. high and 10 ft. in diameter. Each cistern has a false perforated bottom, covered with blanket, upon which the bone-char rests, the blanket serving to prevent any char dust passing out with the treated syrup, which should be perfectly transparent owing to the previous filtration in the bag-filter. The rate of flow through the char cistern is so adjusted that the liquor may be sufficiently long in contact with the char to thoroughly utilise its power of removing the colouring matter and certain organic matters from solution. As long as the liquor leaving the char is colourless, it is allowed to flow into the same tank and is used for making white refined sugar. When, however, the liquor begins to assume a yellowish tint, it is diverted into another tank, and is used for producing a lower grade of sugar. It is usual to proceed in this manner until the liquor passing away from

the cistern is of a light orange colour. The liquor inlet is then turned off, and hot water is run on to drive out the solution of sugar, but as the water mixes to some extent with the liquor a quantity of weak sugar solution is always made. This is known as 'char water,' and is



(Elevation.)

A. Blow-ups. B. Taylor filters. C. Raw sugar tanks. D. Char cisterns. E. Char kilns. F. Char trucks. G. Char elevators. H. Fine-liquor tanks. I. Sweet-water tanks. J. Washing tanks.



(Plan.)

A. Blow-ups. B. Taylor filters. C. Raw sugar tanks. D. Char cisterns. E. Char kilns. F. Char trucks. G. Char elevators. H. Fine-liquor tanks. I. Sweet-water tanks. J. Washing tanks.

FIG. 16.—MELTING AND CHAR DEPARTMENTS OF A SUGAR REFINERY.

employed in dissolving raw sugar, or, owing to its turbidity and the impurities it contains, is treated separately from the other liquors. It is usual to start a char cistern with good liquor, and afterwards to follow this up with lower-quality liquors. The char water flows into

the liquor tanks when above 18°Be. , or as long as it remains bright. When this ceases to be the case, it is run into other tanks until its density is reduced to 1° or 2°Be. , and when this point is reached it is no longer worth saving, and is therefore run down the drain. The washing of the char with boiling water is continued for some hours so as to remove, as far as possible, all organic and other impurities. The char is then allowed to drain, and is removed from the cistern to be dried and re-burnt, or, as it is termed, 'revivified,' in the char kilns.

The kilns employed for this purpose may be divided into two classes, viz. revolving kilns and pipe kilns. The first consist of cast-iron cylinders, revolving in an inclined position and heated externally by fire, through which the char is passed continuously, being turned over in its passage by lifting shelves, and discharged at the lower end into an air-tight chamber. These kilns have of late been almost entirely

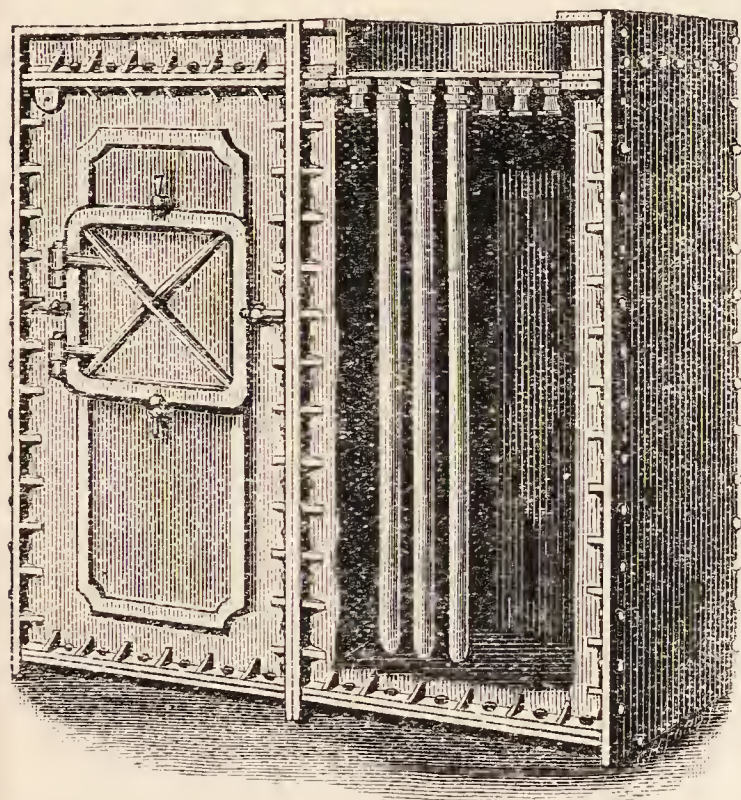


FIG. 17.

replaced by the pipe kilns, of which various modifications are employed, one of the best being shown in Fig. 18. In this apparatus the char is introduced through the two hoppers at the top, first into drying pipes, then into the retort pipes, where it is heated uniformly to a temperature of about 1050°F. , and finally into the cooling pipes, from which it is passed into an automatic discharging apparatus, being drawn off in measured amounts at given intervals of time. After revivification the charcoal is conveyed by a travelling band and elevator to a hopper placed above the char cistern.

Decolorising carbon which has been used for decolorising sugar solutions may be regenerated by treatment with activating gases at high temperatures, which, however, need not be so high as those used in the original production of the charcoal from carbonaceous material. Suitable gases include superheated steam, carbon dioxide, retort or generator gases, oxidising gases, and combustible gases, such as carbon monoxide or hydrogen, mixed with suitable quantities of air, whilst chlorine, sulphur

dioxide, and similar gases may be used for removing inorganic impurities. During the treatment, the charcoal is (a) agitated mechanically, *e.g.* by a conveyor which lifts the particles and drops them through a current of the gas fed into a heated drum, or (b) maintained in a state of flotation by means of a blast of the gas introduced, *e.g.* into the bottom of a vertical retort in such a manner as to carry the granules upwards, the supply of activating gas being reinforced, if necessary, by the addition of non-reacting gases (General Norit Co., Ltd., Assees.

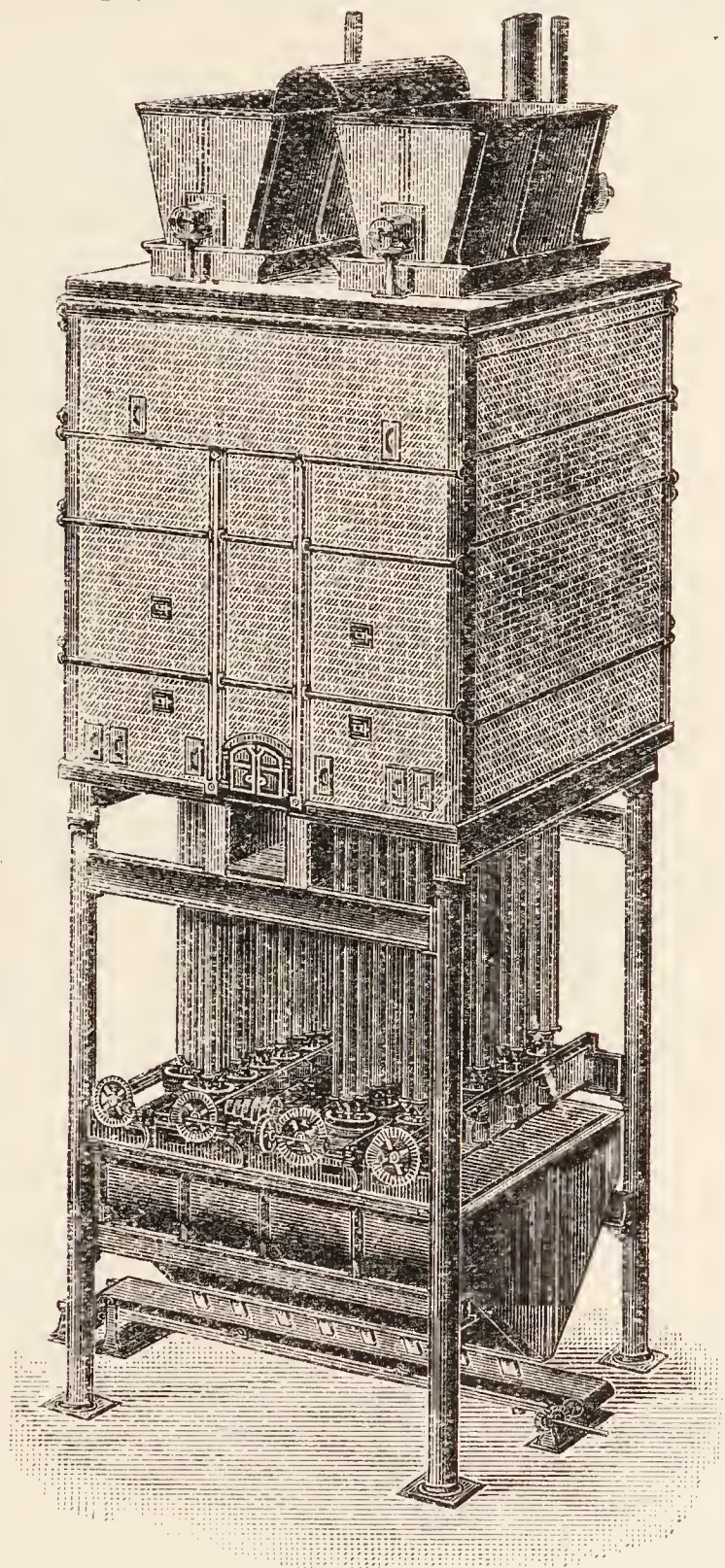


FIG. 18

of J. N. A. Sauer, Eng. Pats. (a) 213939 and (b) 213940, January 13, 1923; Conv. May 5, 1922; J. Soc. Chem. Ind. 1924, 43, B. 608).

(5) *Boiling to grain.*—The colourless and transparent liquor leaving the char is now ready for crystallisation by evaporating the contained water in the vacuum pan (Fig. 10). According to the variety of refined sugar to be made, the pan boiler has merely to produce crystals of the required size. Thus for 'granulated sugar' medium-sized crystals are obtained in the manner previously described for raw beet sugar.

'Crystal sugar' is produced by causing the 'granulated' crystals to grow in the following manner. After a 'strike' of 'granulated sugar' has been boiled in the pan, about three-quarters are discharged, fresh liquor drawn in, and the boiling continued. The sugar crystallising from the fresh liquor is deposited on the medium-sized crystals left in the pan, causing them to grow, and this growth continues until the pan is once more filled. Three-quarters are again discharged, and the remainder boiled with fresh additions of syrup, these operations being repeated until the crystals attain the desired size. This mode of operating is termed 'cutting the pan,' and each portion discharged from the pan is called a 'cut.' Consequently each successive 'cut' contains crystals of increasing size. During the boiling of each 'cut' great care and skill are necessary to prevent the formation of new

crystals, termed 'false grain,' and the boiling temperature is regulated between 160° and 190°F. Very small crystals are required for producing 'castor,' 'loaf,' and 'cube' sugars. In this case a large quantity of liquor is drawn into the empty pan, and rapidly concentrated to 'grain-ing point.' The pan is thus about half filled when the crystals are first formed, and, owing to the immense number of minute crystals, their individual growth is extremely slow during the time that the pan is filling. The entire contents of the pan are then discharged, and the pan is re-started with fresh liquor. The boiling temperature is regulated between 120° and 140°F.

A pan or 'strike' of 'crystal sugar' takes about three times as long to produce as a 'strike' of fine-grained sugar, due to the difference in the rate of boiling. The massecuite after leaving the pan is usually heated in steam-

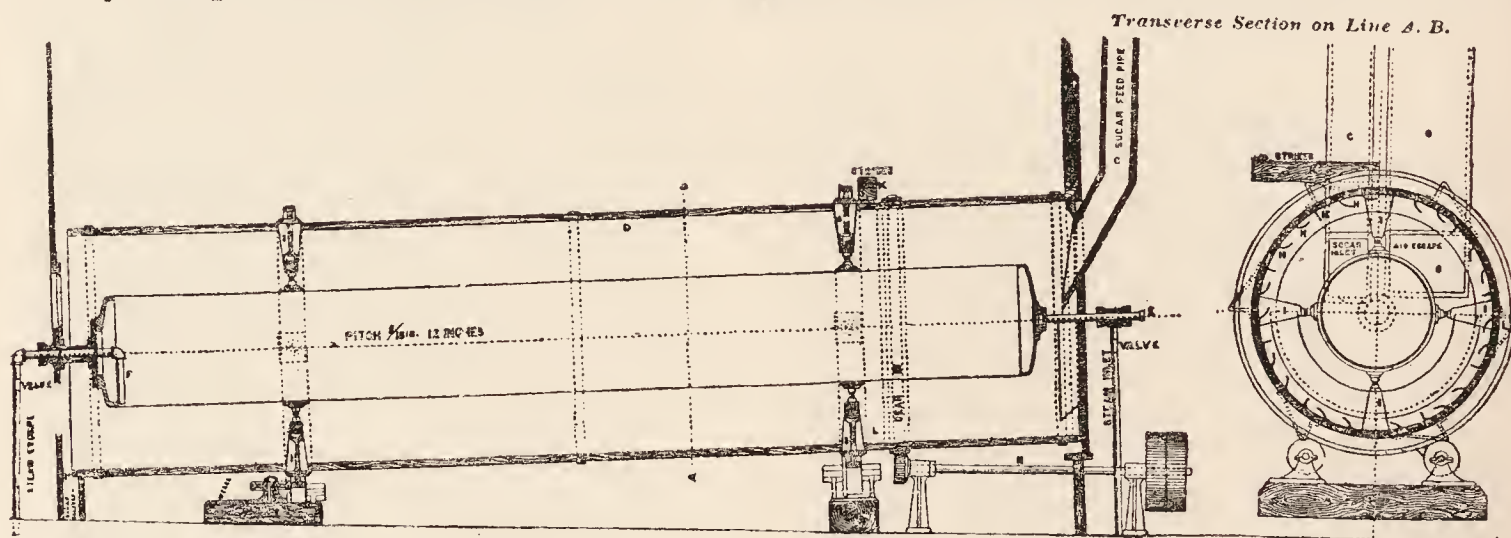


FIG. 19.—HERSEY GRANULATOR.

jacketed vessels, fitted with stirring gear, in order to increase its fluidity and thus prepare it for the next process.

The foregoing operations (1) to (5) represent the routine work of the refinery up to the formation of crystals in the vacuum pan. The subsequent operations differ according to the variety of sugar to be made.

(a) GRANULATED, (b) CRYSTAL, (c) CASTOR.

(6) *Separation of the crystals.*—The massecuite is spun in the centrifugal machine (Fig. 11) previously described. After the 'green syrup' has thus been separated, a little water is sprayed over the sugar whilst the machine is running to wash out the last trace of syrup, which would otherwise impart a yellow tint to the crystals.

(7) *Drying the crystals.*—In order that the sugar may be perfectly granular, the adhering moisture is removed by passing the crystals through a hot-air drier. The 'Hersey granulator' (Fig. 19) is used in nearly every refinery in the United States and Canada and in many refineries in Europe. It consists of an inclined cylinder or drum, slowly rotated on its axis. Sugar enters through a hopper at the higher end, slowly travelling through the drum until it is discharged from the lower end. Along the axis of the drum is a cylindrical chamber filled with steam, and which rotates in unison with the drum. The interior of the drum is fitted with 'lifting shelves,' so that at every revolution the sugar is raised and dropped upon the steam-heated chamber, and, whilst falling, is exposed to a current of air blown through the drum. On

leaving the drum it falls upon a sieve which separates it into different grades, each grade consisting of crystals of uniform size. The sugar is then ready for packing.

(d) LOAF SUGAR.

A massecuite of small crystals is heated to about 180°F. and run into conical sheet-iron moulds arranged in rows, the cones being inverted and closed at the lowest point or 'nose' by wooden spigots. The filled moulds remain in the fill-house from 10 to 12 hours, during which their contents are stirred until the mass becomes thick and there is no danger of the crystals settling out and so rendering the loaf of unequal texture. When their contents are set, the moulds are removed to one of the upper floors of the refinery, the plug closing each mould is removed, and a pointed iron rod inserted into the sugar to the depth of 2 or 3 ins. to facilitate the drainage of the syrup. The moulds are next placed in holes in racks or stages, and the so-called 'green syrup' drained away into gutters placed beneath. The stages are generally made of wood, and the holes are arranged at such a distance apart that the rims at the top of the moulds may touch and afford mutual support. After remaining on the stages for about 24 hours the green syrup ceases to run, and the soft upper surface of the sugar is removed, and mixed with a perfectly colourless and nearly saturated solution of sugar (fine liquor) forming a magma which is then replaced in the mould, thus making a flat, porous surface, through which the fine liquor, afterwards employed for washing the

sugar, passes in a slow even stream. When the surface of the magma has become dry more fine liquor is run on, and this operation is repeated several times until the syrup running away is colourless. The cones are then allowed to drain until only a few inches of the pointed ends remain moist, and are removed from the moulds by inverting the latter and striking them on the rim against a hard block of wood. Each loaf is next placed on its base, in racks, one above the other, heated by steam pipes or hot air to about 120°F. The time occupied in these

various operations depends upon the quality of the raw sugar employed, and the grain of the fine sugar produced, but generally occupies from 10 to 14 days, about half this time being required for drying.

(e) CUBE SUGAR.

With a view to more rapid modes of working, numerous inventions have been brought out and patented. These may be divided into two classes, (1) those producing moulded sugar from massecuite in the form of slabs or sticks; and

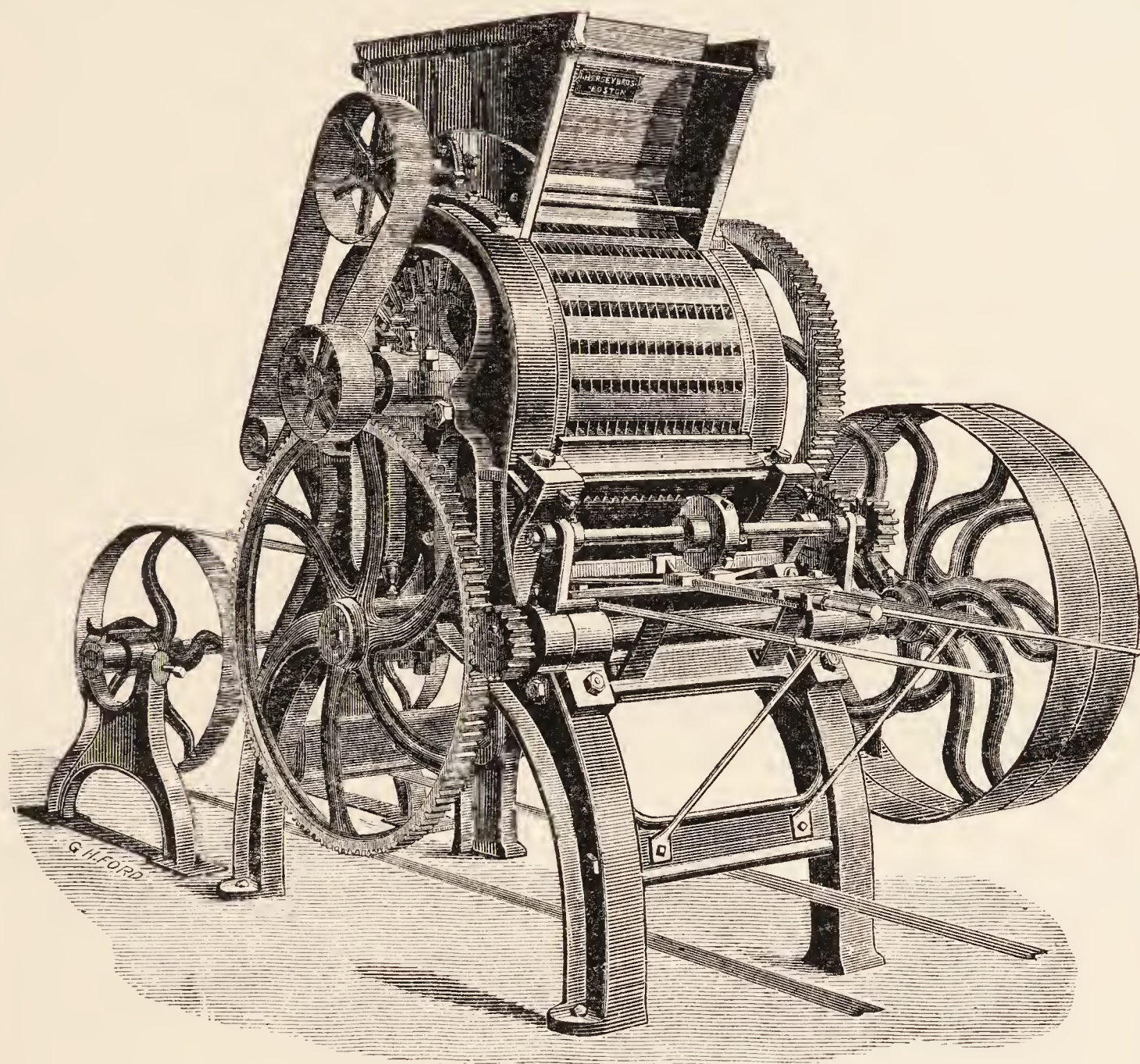


FIG. 20.—HERSEY CUBE MACHINE.

(2) those producing sticks or cubes of sugar, by means of pressure, from soft white sugar which has been dried and purified in a centrifugal machine. Under the first-named category, the most important is Langen's process. In this the massecuite is run into small segmental moulds divided every $\frac{3}{4}$ in. or so by means of movable iron plates. The moulds are placed one upon another, with a perforated plate, the edges of which are covered with cloth, to make a joint, and are filled, and allowed to remain till the sugar has set, when the moulds are taken apart and the slabs placed in a special centrifugal machine, by which the green syrup is removed. They are then placed in another centrifugal machine, in which the sugar slabs are washed by fine liquor, this process being repeated, if necessary, or these two operations are sometimes effected in the same machine. The

sugar slabs are afterwards dried in a stove and cut up into cubes. In the Adant process, a modification of Langen's, the principal advantage is that the slabs are placed edgewise in the centrifugal, their removal thus being rendered easier. Duncan and Newlands have also devised a plan of producing moulded sugar, in the form of sticks, which has been somewhat largely used.

(2) The processes used for making pressed cubes are those of Hersey and of Pzillas. The Hersey cube machine is shown in Fig. 20. Perfectly white moist sugar from the centrifugal machine is fed into the hopper at the top of the machine, and is then automatically mixed with a small quantity of liquor, just sufficient to cause the grains to bind together. At the bottom of this hopper is a hollow revolving drum, in the periphery of which are rows of moulds, each of

the size of the cube it is intended to make. These moulds are open externally, but are closed internally by movable plungers connected together by iron bars placed parallel with the axis of the drum, and caused to advance or retreat by means of a cam arrangement. The sugar falls from the hopper into the row of moulds which happens to be under it, and in which the plungers are withdrawn by the action of the cams to their fullest extent. As the drum moves another row of empty moulds receive their charge. The full moulds pass behind an iron 'press plate,' extending about half way round the drum, which closes the exterior openings, and against this plate the sugar is gradually squeezed, by means of the plungers, until the filled moulds reach the bottom of the press plate, when the cubes are pushed out in rows on to small tin plates, which are carried on a band moving in unison with the drum. The plates containing the soft moist cubes are then placed in a stove heated by steam pipes, and the sugar on drying becomes hard enough to pack into barrels. The greater portion of the hard sugar consumed in the United States is made by this process. One machine will convert 250 tons of soft sugar into cubes weekly, with a comparatively small amount of manual assistance.

The Pzillas cube machine, which is largely used on the Continent, was invented prior to that last-described, and resembles it in many respects. The sugar, however, is turned out in the form of sticks, and requires to be cut into cubes by means of a cutting-machine. This latter consists of a table on which the sticks, after being arranged side by side, are moved by an endless band, passing on their journey between knives having a reciprocating movement, causing them to cut the sugar into cubes or tablets. Other machines have been devised for pressing sugar, but have not come into general use.

(f) ICING SUGAR.

The waste portions and odd pieces of loaf and cube sugars are converted into icing sugar by grinding in mills, followed by sifting.

(g) YELLOW CRYSTALS.

These are manufactured either from refined 'granulated' or from raw beet sugar of superior quality, which is first washed with steam or water in centrifugals. The sugar is spread over a clean floor in a layer of about 1 ft. in depth, and is sprinkled with about 2 p.c. of its weight of a mixture of 'golden syrup' and yellow dye, such as 'golden bloom.' The sugar is then turned over with shovels until a uniform mixture results, which is bagged off in a moist condition. A better method is to mix the sugar, syrup, and dye in a special apparatus fitted with stirring-gear.

(h) SOFT PIECES.

This is an inferior quality of refined sugar produced by re-boiling the 'green syrup' separated from the white sugars in the centrifugals. It is of lower purity than the raw sugar entering the refinery, and may almost be regarded as a by-product. It may be rendered lighter in colour than raw sugar by passing the 'green syrup' over bone char before it is re-boiled in the vacuum pan.

By-products of the refinery.—When the refinery 'liquor' or syrup has been repeatedly boiled and crystallised, an uncrystallisable residue is obtained, called 'treacle,' which corresponds to the by-product called 'molasses' of the raw sugar factory. The former is, however, much purer than the latter, and is used as human food, whereas molasses is only suitable for cattle food. Treacle is also 'refined' by passing it over bone char to render it lighter in colour.

'Golden syrup' differs essentially from refined treacle, in being a manufactured article, and in no sense a by-product.

In many Scotch and in some English refineries the centrifugal syrup resulting from each day's work is returned to the melting-pans on the following day. This system favours rapid working, but is only successful when treating raw sugar of superior quality. It yields a first, second, and sometimes a third grade of white sugar, and two or three lower grades. The first grade product is often ready for sale the day after the raw sugar has entered the refinery, and the remaining products are obtained within two or three days.

Recent progress in sugar refining relates to the use of decolorising carbons, possessing about 30 times the bleaching power of bone char. These new carbons are described under *Decolorising carbons*, two well-known varieties being the Dutch product 'Norit,' and the German product 'Eponit.'

Although substituted for bone char, the method of using these carbons differs entirely from bone-char practice, as described above. In the first place, a much smaller quantity of carbon is required to decolorise a given weight of syrup or liquor, and the carbon can act on the syrup by merely mixing the two together in a vessel fitted with stirring gear. After acting, the carbon can be rapidly separated from the syrup in a filter-press, washed therein with water, and used again for decolorising fresh portions of syrup, the operations being repeated until the activity of the carbon becomes too much reduced (as in the case of bone char).

It is then revived by boiling it with dilute caustic soda solution, separated in a filter-press and washed with hot water to remove the alkali. The carbon is thus revived by a wet treatment, whereas bone char must be roasted in a furnace.

The 'carbon process' dispenses with the cumbrous char cisterns, char kilns, and Taylor filters. It has been used in refineries, and also in raw beet sugar factories in Holland.

According to the annual report for 1922 of the American Sugar Refining Co., the world's estimated output of cane and beet sugar during 1922-23 amounted to 17,988,925 tons, as compared with 17,637,728 tons in 1921. Of this amount 12,659,635 tons represented cane sugar and 5,329,290 tons beet sugar, the totals in the previous year being 12,657,786 tons of cane and 4,979,942 tons of beet sugar. The United States production of cane and beet sugar in the year 1923 was estimated at 1,674,875 tons (cane 1,049,875 tons, beet 625,000 tons), as compared with 2,061,221 tons (cane 1,150,031 tons, beet 911,190 tons) the previous year. Imports of full-duty sugars in 1922 totalled only 47,301 tons, against 198,638 tons and 885,868 tons, respectively, in 1921 and 1920. The chief

sources of supply in 1922 were: Mexico, 19,623 tons; Nicaragua, 8501 tons; Guatemala, 4809 tons; Honduras, 4144 tons; Peru, 2804 tons; and Venezuela, 2481 tons. Exports of refined sugar during the same period amounted to 819,964 tons (416,881 tons in 1921, 412,494 tons in 1920), and the chief destinations included the United Kingdom, 268,275 tons; France, 150,810 tons; Germany, 47,528 tons; Norway, 32,864 tons; Greece, 32,354 tons; Turkey, 27,212 tons; the Netherlands, 26,044 tons; Spain, 25,361 tons; Belgium, 23,190 tons; Italy, 22,316 tons; Argentina, 21,964 tons; Uruguay, 15,837 tons; British India, 12,455 tons; and Egypt, 12,218 tons. Exports in 1922 went to 83 foreign countries, the amount being practically equal to the 885,868 tons imported into the United States from nearly 50 foreign countries in 1920. It is considered that the export trade could be increased to a million tons per annum without curtailing domestic requirements (Bd. of Trade J. April 5th, 1923).

It was estimated that during 1923-24 season, 95 beet-sugar factories would be operated in France, and that the production would be 480,000 metric tons of sugar, compared with a yearly consumption amounting to 700,000-800,000 tons. In 1923 the area cultivated was 150,000 hectares, and the output of sugar in 90 factories was 445,000 tons. In 1913-14 there were 209 factories, with a total production of 785,550 tons from 229,000 hectares, and the consumption was 710,000 tons (J. Chem. Soc. Ind. 1923, 42, 1190).

World's Beet Sugar Production.—The following table shows the area under sugar beet and the production of the roots in 1921 and 1922 in various countries:—

Country	Area (1000 acres)		Production (1000 metric tons)	
	1922	1921	1922	1921
Germany .	1,129	1,086	10,791.6	7,979.8
Belgium .	148	143	1,695.4	1,462.9
Bulgaria .	25	20	213.8	173.4
Denmark .	60	88	573.0	868.6
England and Wales .	8	8	—	—
Finland .	2	2	11.5	13.0
France .	286	298	2,873.3	2,060.6
Italy .	222	158	2,260.0	1,751.3
Netherlands .	143	183	1,846.2	2,708.3
Austria .	27	20	176.7	93.8
Poland .	269	196	2,671.4	1,128.8
Rumania .	54	57	—	351.6
Sweden .	41	121	456.5	1,484.6
Switzerland .	2	2	34.0	42.4
Yugoslavia .	49	41	—	188.5
Spain .	110	133	—	1,816.4
Czechoslovakia .	519	544	5,240.1	4,071.7
Hungary .	90	103	573.4	542.9
Canada .	20	30	156.9	243.1
United States .	535	810	4,744.6	6,965.3

It will be noticed that most European countries increased their output of sugar beet in 1922, even where a decrease in the acreage is shown (J. Soc. Chem. Ind. 1923, 42, 1013).

Literature of Sugar Refining.

Books.—L. S. Ware, Beet Sugar Manufacture and Refining (Chapman and Hall, London, 1907); Newlands Bros., Sugar (Spon & Co.,

London, 1909); Gredinger, Die Raffination des Zuckers (Hartleben's Verlag, Vienna and Leipzig, 1908); T. H. P. Heriot, The Manufacture of Sugar from the Cane and Beet (Longmans, London, 1918).

Journals.—See under Literature of Cane and Beet Sugars. T. H. P. H.

SUGAR ANALYSIS.

The methods to be described in this article are selections from the most modern, the majority of which have been found to give accurate results in the writer's hands. Since they are all empirical it has been necessary to give a large number of tables, which, however, in most cases, have been condensed from the originals, so that intermediate values must be obtained by interpolation.

Qualitative reactions of the sugars.—The power of reducing alkaline solutions of metallic salts (see pp. 461, 469) and that of forming phenylosazones (see p. 478), are exhibited by those sugars which contain a free carbonyl group. Some of the latter class of sugars form characteristic phenylhydrazones. Thus the phenylhydrazones of mannose, fucose, rhamnose, and rhodose are very insoluble and separate almost immediately when a solution containing equal parts of phenylhydrazine and 50 p.c. acetic acid is added to a cold aqueous solution of any of the above sugars. The use of substituted derivatives of phenylhydrazine as reagents for identifying different sugars is often of service both as regards the formation of hydrazones and of osazones. Methylphenylhydrazine gives a characteristic osazone with lævulose, and has been shown by Ofner, contrary to previous statements, to form an osazone with dextrose or mannose. The sugars also give characteristic colour reactions with different phenols. For a description of these and other reactions the reader is referred to the article on CARBOHYDRATES (vol. ii. p. 24).

Polarimeters.—The theory and construction of polarimeters are dealt with in a special article on POLARIMETRY (vol. v. p. 336). The article, however, deals exclusively with instruments in which the rotation of the plane of polarised light is measured by rotating the analyser, and no description is included of those instruments, exclusively used in sugar technology, in which the rotation is measured by quartz compensation. These instruments are generally known as saccharimeters, because their use is restricted to sugars, and more especially to sucrose (cane sugar), for which they were originally designed. It was the French physicist, Soleil, who in 1848 devised a method of determining the strength of sugar solutions polarimetrically by quartz-compensating instruments, thus obviating the use of monochromatic light, which presents many inconveniences and difficulties in practical work. Soleil's method was based on the fact that the rotation of the plane of polarised light by solutions of sucrose and by solid rock crystal (quartz) respectively, runs approximately parallel for light of different degrees of refrangibility. In other words, solutions of sucrose and solid rock crystal have substantially the same rotatory dispersion. Soleil therefore constructed an instrument in which the polariser and analyser

were fixed, and in which the rotation of the plane of polarised light by a sugar solution could be compensated by means of a definite thickness of quartz rotating the plane in the opposite direction.

The principle of the method of compensation may be seen by the aid of the following diagrams.

In the single-wedge system, Fig. 21, the plate A of dextro-rotatory quartz is stationary, whilst the wedge B of lævo-rotatory quartz is capable of being moved in a lateral direction, and the wedge C of lævo-rotatory quartz is

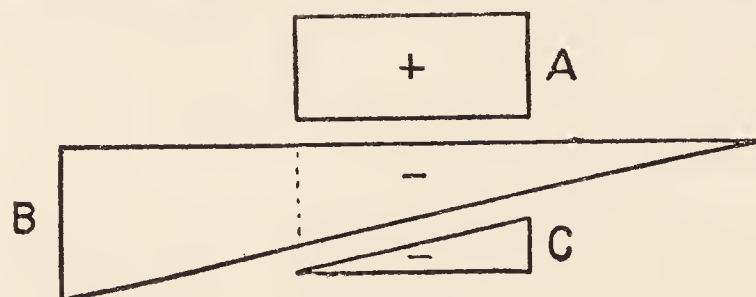


FIG. 21.

again stationary. The system as arranged in the diagram is at the zero-point, that is to say the two lævo-rotatory quartz wedges exactly compensate the dextro-rotatory quartz plate. If now a dextro-rotatory sugar solution is placed in the instrument and the equilibrium thereby destroyed, the movable lævo-rotatory quartz wedge B is moved from left to right until the alteration caused by the sugar solution is exactly compensated. Obviously by employing a plate and wedges the rotation of which is of opposite sign, an instrument for lævo-rotatory sugars might be constructed.

The double-wedge system, Fig. 22, is adapted for either dextro- or lævo-rotatory sugars. It will be seen that in this system there is no quartz plate but two small wedges A and D of

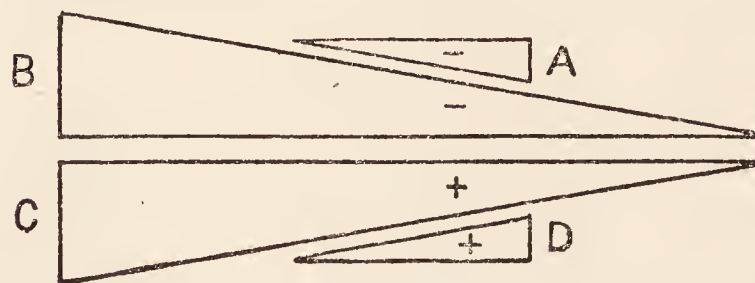


FIG. 22.

opposite rotation, which are fixed, and two large wedges, B and C, also of opposite rotation, which can be moved in a lateral direction as already explained.

The earliest instruments to which the principle of quartz compensation was applied were the Soleil-Duboscq in France, and the Soleil-Ventzke-Scheibler in Germany. In both these instruments the measurements are made in terms of the mean yellow ray. Two half discs of quartz of opposite rotation, cut perpendicularly to their optic axes, and each having a thickness of 3.75 mm., are cemented together. If such a plate be interposed between two Nicol prisms the principal planes of which are parallel, and white light be passed through the system, the two halves of the field will be of a uniform rose colour, due to the blending of the spectral colours, minus the yellow which is extinguished. The slightest rotation of the analyser (or in the case of quartz-compensating instruments, movement of the quartz wedge) will change one half

of the field to blue, and the other to red, or *vice versa*. This is the so-called transition tint, which is complementary to the medium yellow or *jaune moyen* of Biot. If a sugar solution be placed in an instrument employing this device, the equilibrium in colour of the transition tint will be destroyed and can only be restored by rotating the analyser a certain number of degrees or by quartz compensation.

In former times most of the measurements of specific rotatory power were made in terms of this transition tint, the results being denoted by the symbol $[\alpha]_j$ (j =French *jaune*).¹ For a full discussion of the principle of these instruments the reader is referred to special works. Instruments employing the transition tint have, however, long since ceased to be used generally. Among their disadvantages is the fact that they cannot be used by those who are colour blind, and moreover in sugar technology one of the chief reasons for their abandonment is the difficulty of examining coloured solutions with them.

Modern double-field saccharimeters are the so-called penumbra or half-shadow instruments, employing white light and quartz compensation.

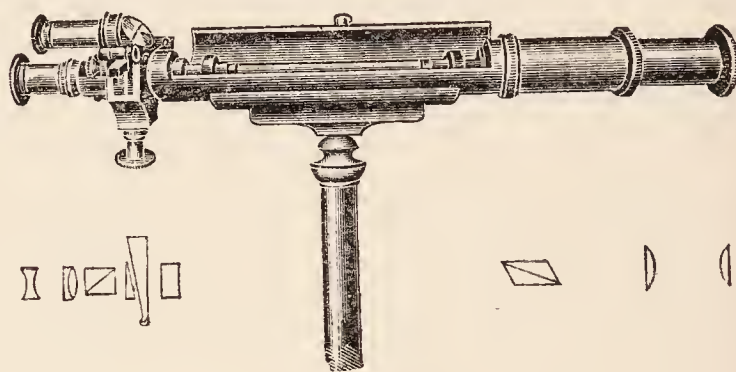


FIG. 23.

Two of these may be mentioned, namely the German instrument of Schmidt and Haensch, and the French instrument of Laurent. The first is constructed for the Ventzke scale, whilst the second employs the French scale. The principles of both these scales will be dealt with later.

In the earliest form of the German instrument, the half-shadow effect is produced by the use of a Jellet-Cornu prism as polariser (Jellet, Report British Assoc. 1860, 13; Cornu, Bull. Soc. chim. 1870, [ii.] 14, 140). An ordinary Nicol prism is divided into halves along its whole length corresponding to the plane of the shortest diagonal. A small wedge $a/2$ is ground from the surface of each half, and the two are then reunited by means of Canada balsam. This makes a double Nicol prism which has two principal planes, making the half-shadow angle a with an ordinary Nicol prism as analyser, the principal plane of the latter being set at right angles to the bisectrix of the principal planes of the divided prism. In the Laurent instrument the half-shadow effect is produced by means of a half disc of quartz (see vol. v. p. 345). The Lippich prism is now more generally used as polariser in the German instrument. By its means a double or a triple field is given (see vol. v. p. 346).

The Schmidt and Haensch half-shadow saccharimeter with Jellet-Cornu prism as polariser is shown in Fig. 23.

¹ For the relation of readings on this scale to those when sodium light is employed, see p. 451.

The more modern form of the instrument, furnished with a Lippich polariser, is shown in Fig. 24. This particular instrument has the double-wedge system of compensation, the wedges being protected in a case.

Saccharimeters are furnished with an arbitrary scale, which gives percentages of sucrose direct when a solution of definite concentration is examined in a tube having a length of 2 dms. The weight of pure sucrose which dissolved in water and made up to 100 c.c. gives a reading of 100 divisions when examined in a 2-dm. tube, is called the normal weight. The German and French instruments employ different normal weights.

Saccharimetry—Ventzke, or German scale.—With the object of dispensing with weighing in saccharimetric work, Ventzke took as his normal solution one of sucrose, which had a sp.gr. of 1.1 at 17.5°/17.5°, his idea being that since such a solution possesses unit excess specific gravity, the percentage of sucrose might be determined in a solution having approximately the concentration of the normal by taking its polarimetric reading in a 2-dm. tube and its specific gravity.

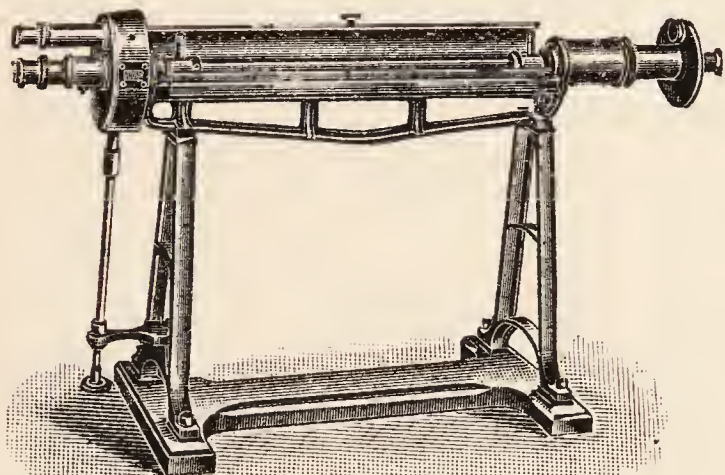


FIG. 24.

It was soon found, however, that as the mineral matters and organic matters other than sucrose present in raw sugars had a different effect on the specific gravity than had sucrose, such a method was inaccurate. A solution of sucrose of the above specific gravity contains 26.048 grms. of sucrose dissolved in water and made up to 100 Mohr's cubic centimetres.¹ The Ventzke normal weight when metric cubic centimetres are employed is 25.9872, or for practical purposes 26 grms. The International Commission, at its third meeting in Paris in 1900, recognising the confusion arising from the two standards of volume, recommended the abandonment of the Mohr for the metric cubic centimetre, and they also recommended that all readings should be made at 20°C. The change in temperature from 17.5°C. to 20°C. necessitated a recalculation of the normal weight owing to the difference in the specific rotations of sucrose and quartz at these two temperatures. The normal weight thus found is 26.0082 grms., and it was decided

¹ The Mohr cubic centimetre, introduced in 1855, is the volume occupied by 1 gram of water at 17.5°C., weighed in air with brass weights. The writer of this article has, for many years, employed the fluid gram at 15.5°C. for all volumetric determinations except those which concern gas analysis. The advantages are that the instruments can be so readily checked, and that specific gravities are usually taken in commercial laboratories at 15.5°/15.5°.

to fix it at 26 grms. Such a solution reads in a 2-dm. tube 100 scale divisions corresponding with 34.657 ± 0.023 degrees of arc with spectrally purified sodium light.

The normal weight used in the scale adopted by saccharimeters of French manufacture was fixed in 1896 at the meeting of the International Congress of Applied Chemistry in Paris as 16.29 grms. of sucrose dissolved in water and made up to 100 metric cubic centimetres at 20°C. If Mohr's cubic centimetres are used the normal weight was fixed at 16.33 grms.

A proposal has been made by C. A. Browne and other American chemists to adopt a sugar scale requiring a normal weight of 20 grms., the principal advantages claimed being: (1) It is a compromise between the German and French weights; (2) the results obtained are easily converted into percentages by multiplying by 5; (3) aliquot portions of 50, 25, 20, and 5 c.c. represent even gram quantities; and (4) the specific rotation of sucrose at a concentration of 20 grms. in 100 c.c. (18.62 p.c. by weight) is about at its maximum. It was further argued that the factor for the conversion into degrees of arc, namely $100 = 34.657$, has been shown by Bates and Jackson (1916) to be inaccurate, so that it would be opportune to adopt a new factor and a new standard. A committee of British chemists drew up a statement of arguments, pro and contra, nearly 2000 copies of which were sent to chemists engaged in the sugar and allied industries throughout the British Empire. Of the replies received 72 p.c. were opposed to the adoption of the new standard. It would therefore appear that British chemists are largely in favour of retaining the present international standard of 26 grms. which in fact is now in almost universal use, excepting in France and Mauritius (see J. Soc. Chem. Ind. 1921, 120, R; Analyst, 1921, 268; Inter. Sugar J. 1921 192).

It is a fact known to all who are engaged in accurate saccharimetric work that the normal weights of different saccharimeters vary, and that it is always necessary to determine the exact weight for each instrument. The German firm, Messrs. Schmidt and Haensch, are, however, particularly careful in the graduation of their scale, as may be seen from the following extract from a letter addressed to C. A. Browne (see A Handbook of Sugar Analysis, 1912, p. 117):—

'The establishment of the scale divisions of our saccharimeters is made at a temperature of 20°C. After fixing the zero-point the linear distance of the 100-degree division is determined by means of a normal quartz plate reading exactly 100 degrees, and standardised at the Physikalisch-Technische Reichsanstalt. This linear distance is then divided into 100 exactly equal parts, the intermediary divisions being also verified by means of corresponding normal standardised quartz plates. The surfaces of the quartz wedges are made perfectly plane, so that a quartz stratum of half thickness corresponds to a half value in the division. Slight errors cannot be prevented, as it is impossible to obtain quartz wedges of the necessary length which are absolutely optically homogeneous throughout. The variableness in the specific rotation of sucrose with concentration of solution is not taken into consideration in the

establishment of the scale division, and this must be corrected for by calculation. Aberrations in the scale division caused by impurities in the quartz can be detected by the control observation tube.'

Verification of the saccharimeter scale.—For this purpose accurately ground quartz plates, standardised by the Physikalisch-Technische Reichsanstalt can now be obtained, but it is obviously prohibitive to purchase a sufficient number of these to check the entire scale. It is, moreover, desirable that this shall be done by means of solutions of pure sucrose of different concentration. Commercial sucrose, although of a high degree of purity, cannot be employed for this purpose, but it must be purified as follows. A concentrated solution of the purest loaf or cube sugar is prepared at the lowest possible temperature. This is further concentrated by evaporation under a partial vacuum, such that the boiling-point never exceeds 80°C. The syrup is then thinned down to twice its volume with a little redistilled commercial alcohol, mixed in a Winchester quart bottle with two to three times its volume of redistilled commercial alcohol, and the mixture vigorously shaken until the crystals separate in the form of a magma. These crystals are filtered from the mother-liquor on a Buchner funnel, washed with alcohol, again dissolved in water,

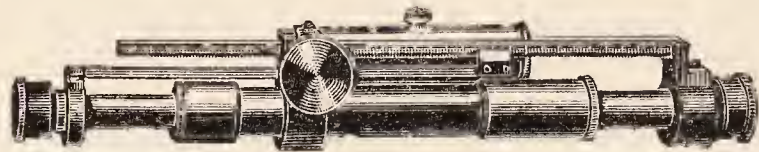


FIG. 25.

and the operations repeated. After two precipitations the sugar is usually pure. It should be dried on a porous plate over sulphuric acid in a vacuum desiccator, and finally heated for a short period at 80°C. The sugar so prepared should then be examined in various ways to ascertain its purity. The mineral matter should be estimated on at least 10 grms. (*see* p. 479), its behaviour towards Fehling's solution should be ascertained, and the specific rotatory power should be determined in a polarimeter making use of sodium light, in which the measurement is made by rotation of the analyser.

The scale having been checked with sugar solutions of different concentration, or by the control tube (*see* below), and the results corrected for the different conditions as described below, any further checking of the instrument can be accomplished by means of standard quartz plates.

One of the most convenient ways of checking the scale of a saccharimeter is by means of the Landolt control tube, the latest form of which, as sold by Schmidt and Haensch, is illustrated in Fig. 25.

The tube can be adjusted to any length from 220 to 420 mm. by means of a telescopic arrangement. The length of a solution is read off on a scale by means of a vernier to 0.1 mm. A funnel is used to receive the overflow of solution as the tube is shortened. For filling the tube the funnel is removed and the opening closed by means of a plug. The tube is then drawn out to its full length, and after moving one of the caps, filled in the usual way.

The following is the method of using the tube. A sugar solution is prepared of such a concentration that it gives a reading of 100 divisions at a length of about 400 mm. This will serve to test the scale at a point a few divisions above 100, and at all points below 100 to 55. For further information the reader is referred to Landolt (*The Optical Rotating Power of Organic Substances*, 1902, p. 441).

In verifying a saccharimeter by means of sucrose, account must be taken of the effect of concentration on the specific rotatory power of that sugar. The useful table shown in the next column has been calculated from the independent experiments of Schmitz and of Landolt by Browne (*Handbook of Sugar Analysis*, 1912, p. 118).

When cane sugar solutions are examined in a quartz compensating polarimeter with white light, errors due to the difference of rotatory dispersion of cane sugar and quartz produced by light of higher refrangibility are introduced. In order to eliminate this source of error Schönrock (*Zeitsch. Ver. Deut. Zuckerind.* 54, 521) suggests that the white light should be filtered through a layer of 1.5 cm. thickness of a 6 p.c. solution of potassium dichromate.

TABLE I.—Effect of Concentration of Sucrose on Saccharimeter Readings.

Scale division	Concentration grams sucrose, 100 true cubic centimetres, 20°C.	Specific rotation sucrose, 20°C.	Actual sucrose value of scale division	
			By Landolt's formula	By Schmitz's formula
100.00	26.00	66.502	100.00	100.00
96.00	24.96	66.506	96.00	95.98
95.00	24.70	66.507	94.99	94.98
90.00	23.40	66.510	89.99	89.97
85.00	22.10	66.513	84.99	84.96
80.00	20.80	66.514	79.99	79.95
75.00	19.50	66.515	74.99	74.94
70.00	18.20	66.516	69.99	69.93
65.00	16.90	66.515	64.99	64.92
60.00	15.60	66.514	59.99	59.92
55.00	14.30	66.511	54.99	54.92
51.00	13.26	66.509	50.99	50.92
50.00	13.00	66.508	50.00	49.92
45.00	11.70	66.505	45.00	44.92
40.00	10.40	66.500	40.00	39.92
35.00	9.10	66.495	35.00	34.92
33.00	8.58	66.492	33.00	32.93
32.00	8.32	66.491	32.01	31.93
30.00	7.80	66.489	30.01	29.93
25.00	6.50	66.481	25.01	24.94
20.00	5.20	66.474	20.01	19.95
15.00	3.90	66.465	15.01	14.96
10.00	2.60	66.456	10.01	9.97
6.00	1.56	66.443	6.01	5.98
5.00	1.30	66.442	5.00	4.98

Effect of temperature.—This effect in the case of a quartz compensating instrument, apart from the change in the specific rotation of sucrose at different temperatures, is threefold as shown by Schönrock (*l.c.*). Thus: (1) the change in shape of the quartz wedge by expan-

sion or contraction; (2) the change in the specific rotation of quartz; and (3) the change due to the expansion or contraction of the material of which the scale is composed. For quartz compensating Ventzke saccharimeters, having a scale of the alloy nickeline, the polarisation value at any temperature P^t of a sugar solution is $P^t = P^{20}[1 + 0.000148(t - 20)]$. When the scale is etched on the quartz wedge, the correction coefficient is 0.000130. C. A. Browne (*l.c.*, p. 127) has compiled some very useful data on the effect of temperature in saccharimetry. He points out that the increase in the rotatory power of quartz with the temperature produces a lowering of the saccharimetric readings, since a lesser thickness of quartz is required for compensation. With sugars which undergo a decrease of rotation with increase in temperature, the combined influences of quartz and sugars are in one direction, and the error introduced may be considerable. Thus with sucrose the temperature coefficient at 10°C. is (0.000148 + 0.000242), at 20°C. it is (0.000148 + 0.000184), and at 30°C. it is (0.000148 + 0.000121).

The following table giving the variation in

the Ventzke reading per 1°C. according to different observers, is quoted from Browne's treatise:—

Andrews (Technology Quarterly, Mass. Inst. Technology, May (1889), 367)	0.0300
The United States Coast and Geodetic Survey	0.0293
Wiley (J. Amer. Chem. Soc. 21, 568)	0.0314
Prisen Geerligs (Archief Java Suikerine, July, 1903)	0.0300
Watts and Tempany (West Indian Bull. vol. iii. p. 140)	0.0310
Average	0.0303

The average temperature coefficient 0.000303 is thus very close to Schönrock's value for 25°C. $(0.000148 + 0.000152) = 0.000300$. For temperatures between 20° and 30°C. the general equation $P^{20} = P^t + 0.00030(t - 20)$ may be used for correcting Ventzke readings to 20°C.

The temperature coefficients of other of the better known sugars for readings on the Ventzke scale have been calculated by Browne, and are given in Table II.

TABLE II.—Temperature Coefficients of Different Sugars of Ventzke Scale.

Sugar	A. $[\alpha]_D^{20}$	B. Change in $[\alpha]_D^{20}$ for 1°C. increase	C. Temperature coefficient $\frac{B}{A}$	Temperature coefficient of reading upon Ventzke scale for 1°C. in- crease. C + coefficient for quartz (−0.000148)	
Fructose . . .	−92.50	+0.625	−0.006757	−0.006905	→ 0
Invert sugar . . .	−20.00	+0.312	−0.015600	−0.015748	→ 0
Lactose . . .	+52.53	−0.070	−0.001332	−0.001480	0 ←
Maltose . . .	+138.04	−0.095	−0.000688	−0.000836	0 ←
Glucose . . .	+53.23	No change.	No change.	−0.000148	0 ←

In the case in which a mixture of sugars is examined in a saccharimeter, the combined influence of the temperature coefficients of each sugar must be taken into account.

In order to obviate errors arising from inequalities of temperature in polarimetric work where great accuracy is required, the readings are conducted in a chamber kept at a constant temperature.

C. A. Browne (*l.c.*, p. 145) has calculated the following useful table, showing the relation between the Ventzke sugar scale, the French sugar scale, and degrees of arc (sodium light)—

Scale.	Equivalent.
1° Ventzke sugar scale = 0.34657°	angular rotation D.
1° angular rotation D = 2.88542°	Ventzke sugar scale.
1° French sugar scale = 0.21666°	angular rotation D.
1° angular rotation D = 4.61553°	French sugar scale.
1° French sugar scale = 0.62516°	Ventzke sugar scale.
1° Ventzke sugar scale = 1.59960°	French sugar scale.

The factor for converting divisions of the Ventzke scale into angular degrees (sodium light), differs slightly for the different sugars. Thus Landolt (Ber. 21, 194) gives the following factors for five sugars—

Sucrose	0.3465
Lactose	0.3452
Glucose	0.3448
Invert sugar	0.3432
Raffinose	0.3450

Brown, Morris and Millar (J. Chem. Soc. Trans. 71, 92) give the following values)—

Sucrose, 10 p.c. solution	0.3469
Maltose, 10 „ „ .	0.3449
„ 5 „ „ .	0.3457
Glucose, 10 „ „ .	0.3442
„ 5 „ „ .	0.3454
Starch products, 10 p.c. solution	0.3458
„ 5 „ „ .	0.3454

Herzfeld (Ber. 28, 441), using a solution containing 11.29 grms. of anhydrous maltose in 100 c.c., found the value of the factor to be 0.3471. For ordinary practical purposes, the writer employs the factor 0.346 for converting divisions of the Ventzke into degrees of arc (sodium light) for all sugars.

For the specific rotatory powers of other sugars the article on CARBOHYDRATES (vol. i. p. 24) should be consulted.

Much of the older work is recorded in terms of the mean yellow ray $[\alpha]_j$ as measured by the transition tint. Indeed, in certain laboratories, transition tint instruments are still in use. To convert degrees $[\alpha]_j$ to degrees $[\alpha]_D$, the former must be multiplied by the factor 0.9. There has been, however, much confusion with regard to what is meant by the medium yellow ray. Thus Brown, Morris and Millar point out (J. Chem. Soc. Trans. 71, 86), that whereas the

original medium yellow ray of Biot was that which was rotated 24° of arc, by a quartz 1 mm. in thickness, as measured by the transition tint, Montgolfier and also Landolt, when dealing with the medium yellow ray, refer to one having a decidedly higher refrangibility with a millimetre-quartz rotation of 24·5°.

The following table gives the rotation of some sugars in angular degrees and in divisions Ventzke as determined by Morris.

TABLE III.—Rotation of some Sugars in 10 p.c. Solution at 20°C.
(According to Morris (J. Fed. Inst. Brewing, 1898, 4, 174).)

	$[\alpha]_D$	Reading in a 2 dm. tube in the half-shadow polarimeter employing white light. Ventzke divisions for 1 gram of sugar in 100 c.c.
Dextrin	202·0°	11·66
Maltose (anhydrous)	138·0°	7·97
Cane sugar	66·5°	3·84
Dextrose	52·8°	3·05
Lævulose	−92·0°	−5·31
Invert sugar	−19·6°	−1·13

Polarimeter tubes.—The following illustration gives the tube most usually employed with the Ventzke instrument. It will be noticed that

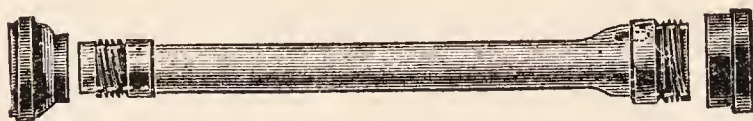


FIG. 26.

one end is considerably wider than the other. The object of this is to obviate the necessity of filling the tube completely, by which work can be conducted in a much more cleanly manner. Air bubbles collect in this wide end of the tube in a position outside of the field of vision.

Polarimeter tubes are usually made of glass,

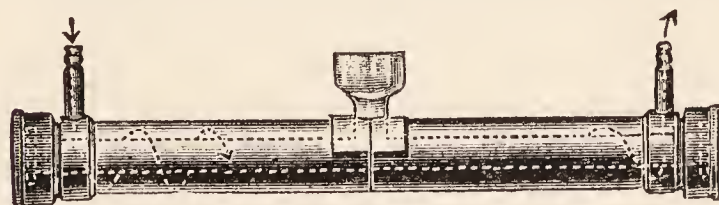


FIG. 27.

but in some cases metal tubes are employed. These latter are not to be recommended on account of the fact that metal has a very much higher coefficient of expansion than glass.

The next illustration shows a tube which is furnished with a brass jacket in order that water may be circulated round the internal glass tube, which is T-shaped. This is for the purpose of controlling the temperature. The tube is filled by a funnel-shaped projection in the middle, which funnel also serves for the insertion of a thermometer to measure the temperature of the solution. Tubes of this kind are used in saccharimetry for the Clerget process (see p. 456).

Methods for the polarisation of raw sugars.—For this purpose the normal weight of the sample is dissolved in water, clarified with basic lead acetate, a little alumina cream added, the solution made up to 100 c.c., and the filtrate observed in a 2-dm. tube. The weighing out of the sugar is conveniently carried out in a special form of nickel boat. It is usual to dissolve the sugar at the room temperature.

Basic lead acetate is prepared in the writer's laboratories as follows: Lead acetate in fine crystals (150 grms.) is mixed in an evaporating basin with litharge (45 grms.) and water (25 c.c.). This paste is allowed to remain at the room temperature for 2–3 hours with frequent stirring. At the end of this time the lead acetate and most of the litharge have gone into solution. It is, however, gently warmed on a piece of wire gauze or a sand-bath by means of a burner. The cream, which is now quite limpid and devoid of colour, is poured into 500 c.c. of water and allowed to remain until the small amount of undissolved sediment settles out. It is desirable to filter the solution. The sp.gr. of the clear filtrate is about 1·20.

Alumina cream is made by pouring a cold 2–3 p.c. solution of alum contained in a pottle bottle into dilute ammonia of sp.gr. 0·98. The converse method of precipitation yields an unsatisfactory granular product. The alumina is allowed to subside and washed in the bottle by decantation twice a day until the supernatant liquid gives no reaction with barium chloride. This usually takes about a week.

The amount of basic lead acetate to be used varies with the kind of sugar. The purest centrifugal sugars require only from 0·5 to 2 c.c.; darker products require up to 10 c.c., whilst molasses require much more. The volume of alumina cream to be used for the normal solution is about 5 c.c.

The following rules were drawn up by the International Commission on Methods of polarising Raw Sugar (Paris, 1900):—

‘In general all polarisations are to be made at 20°C.

‘The verification of the saccharimeter must also be made at 20°C. For instruments using the Ventzke scale 26 grms. of pure dry sucrose, weighed in air with brass weights, dissolved to 100 metric c.c. at 20°C., and polarised in a room, the temperature of which is also 20°C., must give a saccharimeter reading of exactly 100·00. The temperature of the sugar solution during polarisation must be kept constant at 20°C.

‘For countries where the mean temperature is higher than 20°C., saccharimeters may be adjusted at 30°C., or any other suitable temperature, under the conditions specified above, provided that the sugar solution be made up to volume and polarised at this same temperature.

‘In effecting the polarisation of substances containing sugar employ only half-shade instruments.

‘During the observation keep the apparatus in a fixed position, and so far removed from the source of light that the polarising Nicol is not warmed.

‘As sources of light employ lamps which give a strong illumination such as a triple gas burner with metallic cylinder, lens and reflector;

gas lamps with Auer (Welsbach) burner ; electric lamp ; petroleum duplex lamp ; sodium light.

‘Before and after each set of observations the chemist must satisfy himself of the correct adjustment of his saccharimeter by means of standardised quartz plates. He must also previously satisfy himself of the accuracy of his weights, polarisation flasks, observation tubes, and cover-glass. (Scratched cover-glasses must not be used.) Make several readings and take the mean thereof, but no one reading may be neglected.

‘In making a polarisation use the whole normal weight for 100 c.c., or a multiple thereof, for any corresponding volume.

‘As clarifying and decolorising agents use either sub-acetate of lead, alumina cream, or concentrated solution of alum. Bone-black and decolorising powders are to be excluded.

‘After bringing the solution exactly to the mark at the proper temperature, and after wiping out the neck of the flask with filter paper, pour all of the well-shaken clarified sugar solution on a rapidly acting filter. Reject the first portions of the filtrate and use the rest, which must be perfectly clear for polarisation.’

At the seventh meeting of the International Commission for Uniform Methods of Sugar Analysis, which met at the Columbia University, New York, in September, 1912, it was decided that in commercial analyses the use of temperature correction tables should be dispensed with, as far as possible.

Errors attending the use of basic lead acetate as a clarifying agent.—These are threefold, *e.g.* precipitations of certain reducing sugars, especially lævulose,¹ volume occupied by the precipitate, and the fact that in methods of inversion, such as the Clerget method, the stronger hydrochloric acid is replaced by the weaker acetic acid.

Sachs (Zeitsch. Ver. Deut. Zuckerind. 30, 229) has devised the following method for correcting the error due to the volume occupied by the lead acetate precipitate. The precipitate obtained by the clarification of a sugar solution is washed with cold and hot water until free from sugar. It is then transferred to a 100 c.c. flask, half the normal weight of sucrose added, and the solution made up to 100 c.c. The filtrate is

polarised in a 4-dm. tube. The volume of the precipitate is then calculated as follows :—

$$v = \frac{100(P' - P)}{P'}$$

in which *v* is the volume of the precipitate, *P* the polarisation of the sucrose used, and *P'* the polarisation of the sucrose with the precipitate.

Wiechmann (Proc. 5th Inter. Cong. Applied Chem. vol. 3, p. 118) determined the specific gravity of dried lead precipitates from various raw cane sugars in petroleum. His results are given in Table IV.

TABLE IV.

Sugar	Weight of precipitate in grams	Specific gravity $H_2O = 1.00$	Volume in cub. centimetres
Jamaica Muscovado .	0.4559	1.88	0.24
Maceio Muscovado .	0.8112	1.65	0.49
San Domingo centrifugal	0.2525	2.91	0.09
Sandwich Island centrifugal	0.1378	2.84	0.05
San Domingo concrete .	1.0139	3.80	0.27
Porto Rico molasses sugar	0.8959	4.35	0.21
Sandwich Islands	1.0195	4.38	0.23
Cebu mats	1.5400	2.17	0.71
Manila mats	1.3350	2.22	0.60

Horne (J. Amer. Chem. Soc. 26, 186) has suggested the use of dry basic lead acetate to obviate the error due to the volume of the precipitate. This is carried out as follows :—

The normal weight of sugar is dissolved in water in a 100 c.c. flask and made up to the mark without defecation. Small quantities of powdered anhydrous basic lead acetate are added to the solution until the impurities are nearly all precipitated. This point is as easily determined as in the defecation by a solution of the same salt. The organic and mineral-acid radicles in the solution combine with and precipitate the lead and lead oxide of the dry salt, whilst the acetic-acid radicle of the basic lead acetate passes into solution to combine with the bases originally united to the other acid radicles.

The results given in Table V. show the very

TABLE V.

Grade, country	Ordinary polarisation	Specific gravity of precipitate	Volume of precipitate	Corrected polarisation	Dry lead polarisation
Centrifugal	95.0	2.98	c.c. 0.10	94.9	94.9
„ (mixed samples)	94.5	—	0.0765	94.43	94.4
„ Trinidad	96.95	2.91	0.0378	96.91	96.95
„ Java	97.425	2.30	0.0884	97.33	97.375
Muscovado, St. Croix	85.8	1.91	0.4118	85.45	85.5
Molasses sugar, Cuba	89.4	3.20	0.39	89.05	89.0
„ „	89.225	2.85	0.4204	88.85	88.85
„ „	86.45	1.96	0.7108	85.84	85.95
„ „	90.675	3.20	0.3204	90.39	90.45
„ „	89.35	—	0.8500	88.59	88.775
„ „	89.4	3.01	0.4554	88.99	89.0
„ „ Cuba	88.4	2.64	0.4924	87.97	88.0

¹ Compare, however, W. A. Davis (p. 458).

close agreement between the polarisations corrected by the Sachs method, and by the use of dry defecation.

Pellet (Bull. assoc. chim. suc. dist. 23, 285) contends that the increase in polarisation due to the volume of the lead precipitate is not as great as calculated owing to the decrease in polarisation caused by the retention of sucrose in the precipitate which frequently counterbalances the error due to the volume of the precipitate. Horne (J. Amer. Chem. Soc. 29, 926) has since shown, however, that there is no appreciable retention of sucrose when dry basic lead acetate is used in minimum quantity.

A possible error, to which attention has also been called by Pellet, is that any lead which passes into solution by the dry defecation method will increase the volume by its solution.

Hall (Bull. 122, U.S. Bur. of Chem. p. 225) carried out a series of experiments on a Philippine mat sugar to ascertain the effect on the polarisation of increasing amounts of dry basic lead acetate. The lead dissolved in the clarified filtrates was determined and the dilution calculated by allowing an increase in volume of 0.22 c.c. for 1 grm. of dry basic lead acetate dissolved in 100 c.c. of the solution (v. Table VI.).

TABLE VI.

Clarifying agent	Amount of clarifying agent used	In 100 c.c. filtrate		Estimated dilution	Polarisation
		PbO	Basic lead acetate		
		grms.	grms.	c.c.	
Basic acetate solution .	3.0 c.c.	0.2678	—	—	86.70
Dry basic acetate .	0.5 grm.	Trace	—	Trace	Too dark to read
„ „ .	1.0 grm.	0.1530	(0.20)	0.05	86.50
„ „ .	2.0 grms.	0.7203	(0.94)	0.20	86.60
„ „ .	4.0 grms.	2.1078	(2.73)	0.60	86.50

On these results C. A. Browne (*l.c.*, p. 214) remarks as follows:—

‘It is noted that with an estimated dilution of 0.2 c.c. instead of a decrease in polarisation, as would be expected, there is an increase. With an estimated dilution of 0.6 c.c. the reading is the same as that first obtained, so that the combined effect of the dry lead upon the precipitation of fructose, and upon the lowering of the rotation of the fructose in solution is seen to be most pronounced. With sugar-cane products the use of dry basic lead acetate to the point of satisfactory clarification would seem to involve no decrease in polarisation. With low-grade sugar-beet and other products, which are comparatively free from fructose, there is, however, a danger of too low polarisation, since there is no compensating influence for the dilution caused by the excess of lead sub-acetate dissolved.’

It has been shown by Bates and Blake (Bull. U.S. Bur. of Standards, 3, [1] 105) that the presence of a large excess of basic lead acetate solution exerts a large influence on the rotatory power of sucrose. The results given in Table VII. are some of those obtained with normal solutions of sucrose.

Some commercial sugar products can be defecated by a solution of neutral lead acetate, which is generally used as a solution of sp.gr. 1.25. Herles (Zeitsch. Zuckerind. Böhmen, 13, 559; 14, 343; 21, 189) suggested basic lead nitrate as a clarifying agent, especially for low-grade products which are being dealt with by the Clerget method. The replacement of hydrochloric acid by nitric does not influence appreciably the velocity of the hydrolysis of sucrose. The volume of the lead precipitate is, however, largely due to that of the basic nitrate itself, and reducing sugars are precipitated by the reagent.

J. Heron (J. Fed. Inst. Brewing, 1, 113), and also Zameron (Bull. Assoc. Chim. Sucr. Dist. 16, 337), have suggested clarifying sugar solutions with hypochlorite. Insufficient work has been carried out to test the validity of this method, which *primâ facie* does not seem one that could be recommended.

TABLE VII.

Cubic centimetres of basic lead acetate solution (sp.gr. 1.25) per 100 c.c.	Differences in divisions Ventzke between the polarisation of a solution containing no lead, and one containing the volumes of lead mentioned in the first column.
2.0	—0.13
4.0	—0.06
6.0	0.00
8.0	+0.09
10.0	+0.19
20.0	+0.45
40.0	+0.77

There are certain hydrosulphites on the market which are employed in factory work on the large scale for decolorising purposes. Two of these are known by the names of ‘Blankit’ and ‘Redo.’ It has been suggested that these should be used in the laboratory for decolorising sugar solutions. They introduce errors, however, by reacting with reducing sugars to form oxy-sulphonates (*see* Bryan, Bull. 116, U.S. Bur. of Chem. p. 76). Another hydrosulphite derivative, sold commercially as ‘Rongalite,’ is free from this objection. It is sodium formaldehyde sulphonylate.

Purified animal charcoal has been used for decolorising sugar solutions, but the error

the volume occupied by the marc)¹ gives the percentage of sugar in the roots.

It is urged by some that digestion or extraction with alcohol gives more accurate results than the aqueous digestion method; but, taking into account their inconvenience, these methods cannot be recommended for general purposes. It is not necessary to describe here in detail any of these methods; it will suffice to refer to the alcohol extraction method of Scheibler (*Neue Zeits. für Rübenzuckerind.* 2, 1, 17, 287; 3, 242) and the various hot and cold methods of digestion with water and with alcohol respectively.

Estimation of sugar in the juice.—The juice having been expressed by means of a screw press from a sample of the pulp enclosed in a filter cloth, the normal weight is washed into a 100 c.c. flask, 2 c.c. of basic lead acetate solution, and 5 c.c. of alumina cream added, and the liquid made up to 100 c.c. The polarisation of the filtrate in a 2-dm. tube gives the percentage of sugar in the juice.

those of low purity, however (notably with molasses), in which there are many disturbing factors, the influence of which has not been fully worked out at the present time, the errors involved are considerable. In the writer's experience satisfactory results are to be obtained with raw beet sugars which give a direct polarimetric reading of 90 divisions and above on the Ventzke scale,² and with raw cane sugar giving a reading of 94 divisions and above on the same scale.

In the year 1888 a modification of Clerget's method was devised and elaborated by Herzfeld (*Zeits. Ver. Deut. Zuckerind.* 38, 699). It is carried out in the following manner.

The half-normal weight of sucrose is dissolved in 75 c.c. of water in a graduated 100 c.c. flask, 38 p.c. hydrochloric acid (5 c.c.) is then added, and the flask, in which a thermometer is inserted, is placed in a water-bath at 70°C. The flask is shaken continuously, and in this way the temperature of the solution is raised to 67°–70°C. in about 2½ mins., after attaining which, it is kept constant for an additional 5 mins., when it is rapidly cooled and polarised in a water-jacketed tube, 2 dms. in length, at a known temperature. When the polarimetric observation is made at 20°C., and the reading is multiplied by 2 to raise it to that of a normal solution, the value obtained is –32.66 sugar divisions.

The formula including the correction for temperature when the observation is made at a temperature other than 20°C., is—

$$S = \frac{100K}{142.66 - 0.5t}$$

The temperature correction may also be made by Hammerschmidt's formula—

$$I_{20} = I_t + 0.0038K(20 - t),$$

in which I_{20} is the reading of the inverted solution in a 2-dm. tube at 20°C., multiplied by 2, I_t the same at the temperature of observation, and K the difference between the polarisations of the direct and inverted solutions at normal concentration.

If, instead of the half-normal weight in 100 c.c., a solution of a different concentration is employed, the inversion constant varies. Table XI. gives the inversion constants for solutions

TABLE XI.

Sugar, grms. in 100 c.c.	I.	I'.	Sugar, grms. in 100 c.c.	I.	I'.
1	31.85	31.90	11	32.52	32.58
2	31.91	31.96	12	32.59	32.60
3	31.98	32.03	13	32.66	32.66
4	32.05	32.09	14	32.73	32.73
5	32.12	32.15	15	32.79	32.79
6	32.18	32.21	16	32.86	32.85
7	32.25	32.28	17	32.93	32.92
8	32.32	32.34	18	33.00	32.98
9	32.39	32.40	19	33.06	33.04
10	32.46	32.46	20	33.13	33.11

² With these, however, the direct polarimetric reading, as a rule, gives the percentage of sucrose accurately enough for practical purposes.

The specific gravity of the juice is determined by a Brix spindle, observing the usual precautions and correcting for temperature. The principle on which the Brix scale is constructed is explained on p. 482.

Method of estimating sucrose by double polarisation.—The method of estimating sucrose in presence of invert sugar by determining the rotatory power before and after hydrolysis with acid was first suggested by Biot in 1842. It was made practical by Clerget in 1849 (*Ann. Chim. Phys.* [iii.] 26, 175), who elaborated a formula for calculating the results. Clerget's work is to be regarded as classical, and although the details of his original method have been revised, the constants which he established have remained practically unaltered. The method gives very satisfactory results with products of a certain degree of purity. With

¹ This correction is not strictly accurate for all samples, as the percentage of marc is subject to variation.

containing 1–20 grms. of sugar in 100 c.c. The values under I' are calculated by the formula—

$$I' = -\left(31.84 + \frac{i}{20}\right)$$

in which i is the polarimetric reading of the inverted solution in a 200 mm. tube, I being the same multiplied by two.

The corrections for both temperature and concentration are included in the formula—

$$S = \frac{100(P - (-I))}{141.84 + \frac{i}{20} - \frac{t}{2}}$$

P = the direct polarisation.

I = the observed polarisation of the inverted solution corrected proportionately to a normal solution.

$P - (-I) = K$ = the observed Clerget constant at t° ; i = the observed polarisation of the inverted solution in a 200-mm. tube without any correction.

The writer has confirmed the accuracy of these results (J. Soc. Chem. Ind. 17, 110) as Table XII. shows.

The principal factors which affect the accuracy of the Clerget method in raw products are the following. The volume occupied by the precipitate produced by basic lead acetate; the precipitation of lævulose, and to some extent of dextrose, by basic lead acetate; the effect on the rotation of sugars and of certain amino compounds owing to the presence of hydrochloric acid; and the effect (in the case of the most impure products) of the alkali of the basic lead acetate on the rotatory power of lævulose and of certain amino compounds which they contain.¹

Eynon (Seventh Inter. Cong. App. Chem. 1909, Sect. V. p. 193) found that in the case of Jaggery sugar and cane molasses, the influence caused by the volume of the lead precipitate was small but more than that due to the influence of the lead left in solution on the rotation of sucrose.

TABLE XII.

No. of experiment	C = Grms. per 100 c.c.	I_t Found	I_{20}° Calculated from I_t	I_{20}° (from the above table)	Difference between columns 4 and 5
1	2.0	$I_{16} = -33.92$	-31.92	-31.91	+0.01
2	3.0	$I_{17} = -33.05$	-31.55	-31.98	-0.43
3	5.0	$I_{16.5} = -33.92$	-32.17	-32.12	+0.05
4	7.0	$I_{17} = -33.90$	-32.40	-32.25	+0.15
5	10.0	$I_{17} = -33.90$	-32.40	-32.46	-0.06
6	13.024	$I_{17} = -34.10$	-32.54	-32.66	-0.12
7	13.024	$I_{17.5} = -33.80$	-32.53	-32.66	-0.13
8	13.024	$I_{16.6} = -34.20$	-32.47	-32.66	-0.19
9	13.024	$I_{16.5} = -34.50$	-32.72	-32.66	+0.06
10	13.024	$I_{16.8} = -34.28$	-32.65	-32.66	-0.01
11	13.024	$I_{19.6} = -32.60$	-32.40	-32.66	-0.26
12	13.024	$I_{19.6} = -32.88$	-32.68	-32.66	+0.02
13	13.024	$I_{20} = -32.44$	-32.44	-32.66	-0.22
14	13.024	$I_{19.4} = -32.92$	-32.61	-32.66	-0.05
15	13.024	$I_{19.5} = -32.72$	-32.62	-32.66	-0.04
16	13.024	$I_{19.6} = -32.92$	-32.72	-32.66	+0.06

Incidentally Eynon's results confirm those of Prinsen-Geerligs (Internat. Sugar J. 10, 500; 11, 276), that lævulose is partially precipitated (and also dextrose, but to a lesser extent) by basic lead acetate.

It is well known that the velocity of hydrolysis of sucrose by acids varies with the concentration and nature of the acid employed. Strong acids such as hydrochloric acid, which, according to the ionic theory, exist in solution for the most part dissociated into their ions, hydrolyse much more sucrose in a given time, other things being equal, than do the weaker organic acids.

The dark after-products which are met with in the sugar industry, contain, besides sugar, other organic matters, consisting to some extent—in all probability for the most part—of the salts of organic acids. At all events, a sufficiency of these salts is present to react with the hydrochloric acid added in carrying out Clerget's process, and to replace it partially by much weaker organic acids. The matter is not improved when the solution under investigation is previously clarified, as it usually is, with basic

lead acetate, for here the hydrochloric acid is to some extent neutralised by the alkalinity of the basic lead acetate, besides which it is partially replaced by the comparatively weak acetic acid, and there is some danger that the hydrolysis of the sucrose may not have reached completion in the prescribed time. To obviate the presence of an organic acid, it has been proposed by Herles (see p. 454) to use a solution of lead nitrate in conjunction with one of sodium hydroxide as clarifying agent. The experiments of Herzfeld and others have shown, however, that the rotatory power of sucrose is diminished by the employment of this clarifying agent.

There is, however, another objection to the use of Clerget's method, as it is at present carried out, for the estimation of sucrose in products containing much 'other organic matter.' Although the presence of a great many

¹ Andrlik and Stanek have shown (Zeitsch. Zucker-ind. Böhmen, 31, 417), that a 1 p.c. solution of glutaminic acid gave a polarimetric reading of 1.45 Ventzke in presence of basic lead acetate, 0.35 V. in water alone, and 1.77 V. in dilute hydrochloric acid.

definite substances has been demonstrated in the juice of both sugar cane and beetroot, the nature of this organic matter in a given sample of sugar or molasses cannot be determined. It is, however, well known that these substances are to some extent optically active, and experience shows that even after clarification with basic lead acetate some optically active substances besides sugar remain in solution.

Clerget's method presupposes that no other constituent of the sample than the sucrose suffers any change in optical activity by the treatment adopted. But since the agent employed—acid—is a general hydrolyst, we can be by no means certain that this is the case.

It is obvious that if, instead of employing a general hydrolyst such as an acid, we made use of one which would act selectively on sucrose only, the accuracy of the method would be considerably enhanced. Such a hydrolyst is the invertase of yeast, which hydrolyses, or to use the more familiar term, inverts sucrose and other substances having a similar configuration.

O'Sullivan and Thompson (Chem. Soc. Trans. 59, 46) showed that invertase of yeast might be used as hydrolytic agent in the estimation of sucrose; and Ling and Baker (J. Soc. Chem. Ind. 17, 111) proposed a modification of Clerget's method in which the hydrolysis of the sucrose was effected by heating a slightly acidified (with acetic acid) half-normal solution with 0.5 gm. of fresh-pressed yeast for 5 hours at 55°C. Working with pure sucrose in which alumina cream was the sole clarifying agent employed, the Clerget value $I_{20} = -32.56$ was obtained. W. A. Davis and A. J. Daish (J. Agric. Sci. 5, 437; Davis, J. Soc. Chem. Ind. 35, 203) allow the invertase solution to act at 38°C. for 24 hours. They find that under these conditions the Herzfeld constant holds good.

With dark-coloured products defecation with basic lead acetate had to be resorted to, and this was added after the completion of hydrolysis. The method could not, therefore give accurate results under these circumstances, for basic lead acetate affects the rotatory power of certain reducing sugars, notably *lævulose*.

A method of overcoming the difficulty due to the use of lead has been worked out by Ogilvie (J. Soc. Chem. Ind. 30, 62) by removing the lead in solution by means of sulphurous acid prior to hydrolysis. Ogilvie's method is as follows:—

Four times the normal sugar weight of the sample is transferred to a 200 c.c. flask, defecated with the minimum amount of basic lead acetate solution (sp.gr. 1.26), a little alumina cream added, and the liquid made up to the mark at standard temperature, well shaken and filtered. 100 c.c. of the filtrate are measured accurately into a small beaker, sulphur dioxide passed in from a syphon of the liquefied gas till a faint smell is perceptible (the indication that all the lead is precipitated), the liquid is then transferred to a 200 c.c. flask, made up to the mark, and well mixed. Sufficient calcium carbonate (dried) in fine powder to neutralise the excess of acidity, and a little recently ignited kieselguhr are added, after which the solution is filtered. In this way a normal solution is obtained which is sufficiently clarified to give a distinct polarimetric reading, is free from lead

and excess of acidity, and is therefore well suited for the invertase inversion.

The method of hydrolysis is as follows: 50 c.c. of the molasses solution, prepared in the manner just described, contained in a 100 c.c. flask, are raised in a constant temperature bath to 50°–55°C. and 0.5 gm. of washed brewery yeast (top-fermentation) and 2 drops of acetic acid are added, the temperature being maintained as near 55°C. as possible for 4½–5 hours. At the end of this time the liquid is cooled, alumina cream or a little kieselguhr added to assist filtration, and the solution is made up to the mark at standard temperature. The clear filtrate is then polarised in a water-jacketed tube (see Fig. 7) at 20°C., the temperature being determined by a thermometer reading to 0.1°C.

The value obtained by Ogilvie when working with pure sucrose was $I_{20} = -31.6$, a value which, it will be observed, differs from that obtained by Ling and Baker. Cf., however, Davis, *ante*.

W. A. Davis (*l.c.*) points out that the action of basic lead acetate on *lævulose* is not to precipitate that sugar, but to decompose it or to transform it into another carbohydrate of different rotatory and reducing powers (cf. Lobry de Bruyn and van Ekenstein, Rec. Trav. chim. 16, 262).

A preparation of invertase may also be used for the hydrolysis. O'Sullivan and Thompson (Chem. Soc. Trans. 57, 834) prepared invertase by allowing washed yeast to remain aside in a jar until it had liquefied. Fischer (Ber. 27, 2985) found that the autolysis of the yeast might be expedited by the addition of chloroform. C. S. Hudson (J. Ind. Eng. Chem. 2, 143) has proposed the following method of preparing a solution of invertase based on these observations:

'Break up 5 lbs. of pressed yeast, which may be either baker's or brewer's yeast, add 30 c.c. of chloroform to it in a closed flask, and allow it to stand at room temperature (20°C.) overnight. By the morning the solid mass will have become liquid and it should then be filtered through filter paper, allowing several hours for draining. To the filtrate add neutral lead acetate until no further precipitate forms and again filter. Precipitate the excess of lead from the filtrate with potassium oxalate and filter. To this filtrate add 25 c.c. of toluene and dialyse the mixture in a pig's bladder for 2 or 3 days against running tap water. The dialysed solution is colourless, perfectly clear after filtration, neutral to litmus, has a solid content of about one-half of one p.c., an ash content of a few hundredths of one p.c., will keep indefinitely in an ice box if a little toluene is kept on its surface to prevent the growth of micro-organisms, and is exceedingly active in inverting cane sugar. The invertase solution does not reduce Fehling's solution.' Hudson later suggests using toluene instead of chloroform.

W. A. Davis (J. Soc. Chem. Ind. 1906, 35, 202) prepares invertase from autolysed yeast. The pressed yeast is placed in a large wide-mouthed bottle until the latter is nearly full. About 30 to 50 c.c. of toluene is then poured over it and allowed to percolate through the mass. The mouth of the bottle is covered with a sheet of paper and the bottle left in a warm place at a temperature of 25°–30°C. After about a

fortnight the whole of the yeast is liquefied, when it is filtered through a Buchner funnel. The liquid is a highly active solution of invertase, but is quite free from maltase and zymase. Davis finds that Hudson's method of treatment with neutral lead acetate is unnecessary for ordinary purposes of analysis.

Hudson (J. Amer. Chem. Soc. 1914, 36, 1566) suggests the following modification of preparing invertase:—yeast (10 kilos.) is kneaded with water (10 litres) and toluene (500 c.c.). After three days, neutral lead acetate is added until precipitation is complete, the filtrate treated with hydrogen sulphide, filtered, and the filtrate at once thoroughly dialysed in collodion tubes, prepared from collodion solutions of pharmacopæia strength in tubes 35×5 cm. The dialysed solutions are colourless and clear, and show no loss in activity when kept, with toluene, for a month. At the end of a year the activity is reduced to about one-half. Both pressed top yeast and bottom fermentation (brewers') yeast were employed. The latter yields solutions about twice as strong as the former. Liquefaction occurs in a few hours, and on the third day 5 c.c. of the filtered extract (from top yeast) was found to invert half the sucrose in 50 c.c. of a 9 p.c. solution, acidified with two drops of acetic acid and kept at 30°, in 5–9 minutes.

The solution is without action on α -methyl-glucoside, maltose, and lactose. Whilst a solution prepared from top yeast changed the rotation of a solution of raffinose from +123° to +63.9°, a similar solution from bottom yeast changed the rotation from +123° to +14.9°. This is attributed to the presence, in the solution from bottom yeast, of an enzyme (melibiase) which carried the hydrolysis of raffinose to the three hexoses, galactose, glucose, and fructose.

The invertase or yeast process takes up a considerably longer period of time than the acid hydrolysis process, but it must be remembered that it necessitates no more personal attention. However, the writer does not consider that sufficient work has yet been carried out with the method or a sufficient number of low-grade products of the sugar industry examined by it, to render it of general applicability in technological work (*cf.* below). The majority of sugar technologists have been somewhat reluctant to carry out investigations on this enzyme method, and have always shown a preference for the acid method, and numerous attempts have been made to remove the errors inherent to it when dark after-products are being dealt with. Neutralisation of the free hydrochloric acid in the inverted solution by sodium hydroxide, as pointed out by Browne (*l.c.*, p. 271), removes the influence of the acidity, but introduces a new disturbing factor, namely, sodium chloride.

Pellet in 1897 (Bull. Assoc. Chim. Sucr. Dist. 15, 524) proposed to remove the lead in the direct polarisation liquid by sulphurous acid in slight excess, whilst Andrlik and Stanek in 1906 (Zeits. Zuckerind. Böhmen, 31, 417) proposed to add to the direct polarisation liquid the same quantity of hydrochloric acid as is present in the inverted solution together with a certain amount of urea or betaine to retard the hydrolysis of the sucrose by the hydrochloric acid. One objection to this method is that quite an appreci-

able amount of hydrolysis occurs under these conditions even 2 mins. after the preparation of the solution, and a second objection to the method has reference to the effect of the bases employed by Andrlik and Stanek on the rotation of reducing sugars when present. In the case of beetroot molasses which do not contain reducing sugars or at the most only traces, this method appears to give results which agree well with those obtained by the Pellet method (Ogilvie, *l.c.*).

Ogilvie (Internat. Sugar J. 14, 91) has compared the results obtained with invertase and acid hydrolysis respectively in the case of five samples of cane molasses, and arrives at the following conclusions: (1) The percentages of sucrose found by the acid inversion process usually employed when the direct polarisation is taken in alkaline solution are too high.¹ (2) The percentage of sucrose found when using a neutral direct polarisation liquid may likewise be too high. (3) The values found when using an acid direct polarisation liquid are in close agreement with those obtained by the invertase method.

Ogilvie's results with beet and cane molasses are given in Tables XIII. and XIV.

In a later paper Ogilvie (*ibid.* 14, 624) modified the Pellet method of removing the lead from the direct polarisation liquid by means of sulphurous acid, and applied it to the estimation of sucrose in beet molasses by the Clerget process. His procedure is as follows: Twice the normal weight is dissolved in water defecated with basic lead acetate and made up to 200 c.c. with water. Fifty cubic centimetres of this solution are transferred to a 100 c.c. flask, saturated with sulphur dioxide, the flask being immersed in cold water meanwhile, and subsequently made up with water to 100 c.c. and filtered. For the inversion solution 50 c.c. of the defecated normal solution of molasses are transferred to a 100 c.c. flask, 25 c.c. of water added, and 5 c.c. of hydrochloric acid (sp.gr. 1.19), and treated according to Herzfeld's directions (*see* p. 456). Working under these conditions it is shown that the direct polarisation liquid may be kept for 30 mins. without showing any diminution in rotation. This work appears very promising, and further experiments with both beet and cane molasses will be very welcome.

Estimation of sucrose in presence of reducing sugars by a single observation.—Lemeland (Ann. Chim. anal. 15, 416) found that when a mixture of sucrose and reducing sugars is heated with hydrogen peroxide, caustic alkali and a little manganese dioxide, the reducing and optical powers of the reducing sugars are annulled, whilst the optical power of the sucrose is unaffected. Jolles (Zeitsch. Nahr. Genussm. 20, 631) suggests destroying the rotatory power of reducing sugars in admixture with sucrose by boiling 2 p.c. solutions of the mixture for 45 mins. with sufficient sodium or potassium hydroxide to make the solution have a decinormal degree of alkalinity. This method was modified by Pellet and Lemeland (Inter. Sugar J. 13, 616). Cross

¹ Exactly the opposite result was obtained by Ogilvie when working with beet molasses, which, however, as he points out, has a different composition from the cane product. In the former the disturbing factor is the presence of amino acids, whilst in the latter it is the presence of reducing sugars.

TABLE XIII.—*Beet Molasses.*

Sample	1	2	3	4
Direct alkaline (basic lead acetate) polarisation .	48·8	—	48·6	47·0
Direct neutral polarisation	49·2	52·0	49·0	47·6
Direct acid (Andrlik) polarisation	50·4	53·25	50·0	48·4
Direct acid (Pellet) polarisation	50·3	53·3	—	48·3
Invertase inversion polarisation	—14·6	—16·0	—15·0	—14·4
Acid inversion polarisation	—13·2	—14·6	—13·6	—13·8
Clerget value by invertase	48·5	51·7	48·6	47·1
Clerget value by acid, using alkaline direct polarisation	47·0	—	47·1	46·1
Clerget value by acid, using neutral direct polarisation	47·3	50·5	47·4	46·5
Clerget value by acid, using acid (Andrlik) direct polarisation	48·2	51·4	48·2	47·1
Clerget value by acid, using acid (Pellet) direct polarisation	48·1	51·4	—	47·0

TABLE XIV.—*Cane Molasses.*

—	Cuban molasses		Egyptian molasses	Javan molasses	' American syrup '
	No. 1	No. 2			
Ash (sulphated)	6·77	7·34	10·92	10·97	6·05
Reducing sugars	18·71	18·56	11·70	21·98	26·55
1. Alkaline (basic lead acetate) polarisation .	32·20	31·40	39·50	34·30	39·70
2. Neutral direct polarisation	30·50	29·90	38·10	33·46	39·65
3. Acid (HCl and urea) polarisation (Andrlik)	30·50	30·50	38·40	33·38	39·26
4. Acid (SO ₂) direct polarisation (Pellet) .	30·60	30·50	38·30	33·30	39·10
5. Invertase inversion polarisation	—16·40	—15·50	—17·90	—14·08	—11·40
6. Acid inversion (Herzfeld) polarisation .	—16·30	—15·40	—18·02	—14·06	—12·28
7. Percentage of sucrose, using invertase as hydrolyst	35·6	34·4	42·4	36·1	38·7
8. Percentage of sucrose, using acid as hydrolyst, and the alkaline direct polarisation	36·7	35·4	43·4	36·6	39·3
9. Percentage of sucrose, using acid as hydrolyst, and the neutral direct polarisation	35·4	34·2	42·4	35·9	39·2
10. Percentage of sucrose, using acid as hydrolyst, and the acid (HCl and urea) direct polarisation (Andrlik)	35·4	34·7	42·6	35·9	38·9
11. Percentage of sucrose, using acid as hydrolyst, and the acid (SO ₂) direct polarisation (Pellet)	35·5	34·7	42·5	35·8	38·8

and Taggart (*ibid.* 14, 448) state, however, that none of these modifications gives satisfactory results. They find the following procedure to yield good results. A normal (Ventzke) solution is prepared, and 50 c.c. are transferred to a 100 c.c. flask, 6·3 c.c. of sodium hydroxide solution of 36°Beaumé added and 7·5 c.c. of hydrogen peroxide (100 volume). The mixture is cooled to prevent effervescence, and the flask is immersed in a bath of water at 55°F. for 20 mins., cooled, acidified with acetic acid, made up to the mark, clarified with dry basic lead acetate and the rotatory power of the filtrate determined. The reading in a 4-dm. tube gives the percentage of sucrose in the sample. It is shown that the results agree with those obtained by the Clerget-Herzfeld method; and

Cross and Taggart recommend it for syrups and molasses.

Estimation of raffinose in beet products by the Clerget method.—The method of procedure is the same as above described, but the results are calculated by Herzfeld's formulæ (*Zeits. Ver. Deut. Zuckerind.* 40, 194)—

$$S = \frac{0·5124P - (-I)}{0·839}$$

$$R = \frac{P - S}{1·85}$$

where S is the percentage of sucrose, P is the direct polarisation of the normal solution, I the polarisation of the inverted solution at normal concentration, and R the percentage of raffinose. The formula presupposes that the readings have been made at 20°C. If not the temperature corrections given above must be applied. The

following formula should be used for calculating the sucrose when the readings have not been made at 20°C:—

$$S = \frac{P(0.4724 + 0.002t) - (-I)}{0.839 - 0.003t}$$

Estimation of sucrose in presence of other sugars by the Clerget method.—The writer has found that sucrose may be estimated with a fair degree of accuracy in presence of dextrins, maltodextrins, maltose, lactose, or glucose, or of mixtures of these carbohydrates by the Clerget method. The carbohydrates mentioned are for the most part not much affected by the Clerget inversion method; but work on the subject is greatly needed. For the estimation of lactose in chocolate by the Clerget method Dubois has devised a process (Cir. 66, U.S. Bur. of Chem. p. 15; quoted by Browne, *l.c.*, p. 280).

Reduction methods of estimating sugars.—Those sugars which contain within their molecule a free carbonyl group—aldoses and ketoses—are capable of reducing metallic salts in alkaline solution. This is true of alkaline solutions of silver, mercury, and copper salts. In no case, however, does the reduction conform to a definite reaction, so that these reduction methods are all of an empirical character. They must therefore be carried out under standard conditions, otherwise accurate results cannot be obtained. With special reference to cupric salts, the old assumption that one molecule of glucose reduces five molecules of copper oxide has long since been abandoned. Indeed, different sugars under similar conditions reduce different amounts of cupric oxide.

The most important and most widely used of these reduction methods, so far as their quantitative application is concerned, for the estimation of reducing sugars, are those which depend on the reduction of alkaline solutions of cupric salts. Trommer in 1841 (*Annalen*, 39, 360) was the first to show that grape sugar reduced alkaline copper solutions whilst cane sugar did not, and to suggest a method of estimating the former based on this fact. Barreswil, a few years later (*J. Pharm. Chim.* [iii.] 6, 301), showed that the addition of an alkali tartrate to a solution of copper sulphate containing also an alkali hydroxide rendered the reagent more stable. It was not, however, until 1848 that the method of estimating sugars by the cupric reduction method was placed on a sound basis by Fehling (*Annalen*, 72, 106). Fehling's solution, with but slight modifications, is the one most generally employed at the present time.

The first methods of estimating sugars based on their power of reducing alkaline copper solutions were volumetric. Later gravimetric methods were devised. The most recent and widely adopted form of each of these will be considered in what follows.

Volumetric methods.—Passing over the earlier methods based on this principle, the first work on the subject to demand attention is that of Soxhlet in 1878 (*J. pr. Chem.* [ii.] 21, 227). The work of this chemist was of an important character. He was the first to show that Fehling's solution, when kept, underwent auto-reduction, and to suggest keeping the copper sulphate and alkaline tartrate solutions separate and mixing them as required for use. He came

to the conclusion that the volumetric method was capable of greater accuracy than any gravimetric method which was then known. Soxhlet, however, worked with very strong solutions of reducing sugars, and he employed 100 c.c. of Fehling's solution. He also used an open dish for his titrations, which leads to errors on account of the oxidising action of the air (*cf.* Kjeldahl, *Res. Comptes rend. Carlsberg*, 4). The relative reducing powers of the most commonly occurring reducing sugars, according to Soxhlet, are as follows: Glucose 100, invert sugar 96.2, laevulose 92.4, lactose 70.3, and maltose 61.0. These values have been confirmed by numerous observers, but it has to be remembered that the reducing power of a sugar varies according to the conditions under which it was determined.

The end point in the volumetric method was first of all determined by the disappearance of the blue colour, but obviously this could not be used in the case of dark-coloured products. The use of ferrocyanide as an indicator for the unreduced copper was then suggested. It is applied in the following manner: When it is judged that the titration is nearing the end point a little of the liquid is filtered off, the filtrate acidified with acetic acid, and a *freshly prepared* solution of potassium ferrocyanide added, when, if there be any unreduced cupric salt, the well-known brown precipitate or coloration will be produced. Perhaps the most convenient way of ascertaining the end point on this principle is by means of the filter tube (described in Wiley's *Agricultural Analysis*, vol. 3, p. 130). It consists of a piece of glass tubing 20–25 cm. in length and 5–7 mm. in diameter. A shoulder is formed on one extremity, and over this is stretched a piece of fine linen which is fastened on by a piece of cotton. The tube is dipped into water containing finely divided asbestos in suspension, and some of this is drawn into the tube by suction at the open end. This forms a layer which will retain the cuprous oxide produced in the Fehling reducing method.

The volumetric method of estimating reducing sugars has within recent years been standardised by Ling and Rendle (*Analyst*, 30, 183), and Ling and Jones (*ibid.* 33, 160). These chemists performed the titration in an ordinary boiling flask, which, however, had been used by the writer and others many years before the papers cited appeared. The main point which they claim to have established by their work, however, is that of having proved that the volumetric method of estimating sugars is quite as accurate and far more convenient than any form of the gravimetric method.

It may here be mentioned that the composition of the alkaline tartrate solution employed by different chemists varies somewhat, more especially as regards the proportion of sodium hydroxide present. It is well known that the results are largely influenced by the proportion of sodium hydroxide.

The reagent used by the writer and his co-workers is prepared as follows:—

Solution No. 1.—Crystallised copper sulphate (69.2 grms.) is dissolved in water and the solution made up to one litre.

Solution No. 2.—Crystallised Rochelle salt (346 grms.) is dissolved in hot water and mixed

with sodium hydroxide (142 grms.) also dissolved in water. After cooling the mixed solutions are made up to one litre.

Equal volumes of these two solutions are accurately measured out at 15·5°C. or any other standard temperature adopted, and this mixture constitutes the reagent.¹

The method was standardised for a volume of the mixed solution of 10 c.c., but occasionally it is necessary to vary this volume, and Ling and Jones (*l.c.*) show that assuming the concentration of the sugar solution to be constant, the number of cubic centimetres required for any titration is directly proportional to the volume of copper reagent employed—at all events when this lies between the limits of 5 and 20 c.c.

The indicator employed by the writer and his co-workers is an acid solution of ferrous thiocyanate, which is prepared as follows :—

Ammonium thiocyanate . . .	1·5 grms.
Ferrous ammonium sulphate . .	1·0 „
Concentrated hydrochloric acid	2·5 c.c.
Water	10·0 „

The solution prepared even from the purest reagents has invariably a brownish-red colour due to the presence of ferric salt, which latter must therefore be reduced. For this purpose zinc-dust has been found to be the most satisfactory reagent, and, as a rule, a mere trace suffices to decolorise the solution

The method of titration is as follows: The freshly mixed copper reagent (10 c.c.) is accu-

¹ The measurement of equal volumes of these solutions at definite temperatures is a most important point, since the coefficient of expansion of each solution is different and differs also from that of water.

ately measured into a 200 c.c. boiling flask. The reagent, which is not diluted with water, is heated to boiling. The sugar solution, which should be adjusted to such a strength that 20–30 c.c. of it are required to reduce 10 c.c. of Fehling’s solution, is then run into the boiling liquid in small amounts, commencing with 5 c.c. After each addition of sugar solution the mixture is boiled, the liquid being kept rotated. About a dozen drops of the indicator are placed on a porcelain or opal glass slab, and when it is judged that the precipitation of cuprous oxide is complete, a drop of the liquid is withdrawn by a clean glass rod or by a capillary tube, and brought in contact with a drop of the indicator on the slab. The test must be carried out rapidly. It is also essential to perform the titration as rapidly as possible, as an atmosphere of steam is then kept in the neck of the flask and the influence of atmospheric oxygen avoided. At the final point the liquid is boiled for about 10 seconds. As in the ordinary volumetric method, the first titration may only give approximate results, and a second or third will then be necessary to establish the end-point accurately. However, when the operator has gained experience, the first titration is as much to be relied on as succeeding ones, and this point is clearly brought out in the results cited. One titration takes from 2½ to 3 mins.

The copper reagent is standardised against invert sugar as follows: Pure sucrose (0·95 gm.) (*see* p. 450) is dissolved in water (150 c.c.), and boiled with *N*/2 hydrochloric acid (30 c.c.), the mixture being maintained in ebullition for 1 min., cooled, neutralised by the addition of *N*/2 sodium hydroxide (30 c.c.), and made up

TABLE XV.

Volume of solution required by 10 c.c. Fehling’s solution	Dextrose		Lævulose		Invert sugar		Maltose	
	D	D’	L	L’	I	I’	M	M’
	Dextrose in 100 c.c. of solution	Fehling’s solution equivalent to 1 gm. dextrose	Lævulose in 100 c.c. of solution	Fehling’s solution equivalent to 1 gm. lævulose	Invert sugar in 100 c.c. of solution	Fehling’s solution equivalent to 1 gm. invert sugar	Maltose in 100 c.c. of solution	Fehling’s solution equivalent to 1 gm. maltose
c.c.	gm.	c.c.	gm.	c.c.	gm.	c.c.	gm.	c.c.
20	0·2427	206·0	—	—	—	—	—	—
21	0·2332	205·1	—	—	0·2412	197·5	0·3888	122·5
22	0·2226	204·2	0·2411	188·5	0·2311	196·8	0·3711	A constant
23	0·2138	203·4	0·2312	188·0	0·2218	196·0	0·3550	
24	0·2056	202·6	0·2222	187·5	0·2132	195·5	0·3402	
25	0·1981	201·9	0·2138	187·1	0·2052	194·9	0·3266	
26	0·1911	201·3	0·2060	186·7	0·1980	194·3	0·3140	
27	0·1846	200·7	0·1988	186·3	0·1910	193·9	0·3023	
28	0·1784	200·1	0·1921	186·0	0·1846	193·4	0·2915	
29	0·1728	199·6	0·1857	185·6	0·1787	193·0	0·2815	
30	0·1675	199·1	0·1798	185·4	0·1731	192·5	0·2721	
31	0·1625	198·6	0·1743	185·1	0·1678	192·2	0·2633	
32	0·1577	198·2	0·1691	184·8	0·1629	191·8	0·2251	
33	0·1532	197·8	0·1642	184·6	0·1583	191·5	0·2474	
34	0·1490	197·4	0·1596	184·3	0·1539	191·2	0·2401	
35	0·1450	197·0	0·1552	184·1	0·1497	190·9	0·2332	
36	0·1412	196·7	0·1511	183·9	0·1458	190·6	0·2268	
37	0·1377	196·4	0·1472	183·6	0·1421	190·3	0·2206	
38	0·1343	196·0	0·1435	183·4	0·1385	190·1	0·2148	
39	0·1310	195·8	0·1399	183·3	0·1349	189·8	0·2093	
40	0·1279	195·5	0·1366	183·1	0·1319	189·6	0·2041	122·5
41	—	—	0·1334	182·9	0·1288	189·4	—	—
42	—	—	0·1298	182·8	0·1259	189·2	—	—
43	—	—	0·1274	182·6	—	—	—	—

with water to 500 c.c. This solution, which contains 0.2 gm. of invert sugar per 100 c.c., is titrated against 10 c.c. portions of the copper reagent, as above described.

It should here be pointed out that whilst the thiocyanate indicator is by far the most delicate and satisfactory, it cannot be used with commercial products containing iron. With these the ferrocyanide indicator must be employed.

Ling and Jones (*l.c.*) have calculated a table for dextrose, lævulose, invert sugar, and maltose for a range of concentrations such that using 10 c.c. of Fehling's solution the reduction is complete with the addition of 20–43 c.c. of the sugar solution.

The manner of using the table is best explained by an illustration. Suppose a solution of pure lævulose is being examined, and that 25.0 c.c. of it are required to reduce 10 c.c. of Fehling's solution. Opposite 25 in the first column is found 0.2138 in column L; the percentage of lævulose in the solution titrated is thus given direct. If 25.2 c.c., or other quantity not a whole number, is required to reduce 10 c.c. of Fehling's solution, the percentage of lævulose can be easily found by interpolation between the numbers in column L.

The table gives the number of cubic centimetres of Fehling's solution equivalent to 1 gm. of the particular sugar at each concentration. These numbers, given in columns D', L', I', and M', have another purpose—namely, the separate determination of two reducing sugars in a mixture, by a modification of the method of Morris (*J. Inst. Brewing*, 4, 162), which depends on the reducing power and the reading in the half-shadow Ventzke polarimeter when observed in a 2-dm. tube. The application of the table for this purpose is described on pp. 474, 478.

Estimation of invert sugar in presence of cane sugar.—It is well known that sucrose, although by constitution a non-reducing sugar, does reduce Fehling's solution to some extent when boiled therewith, and that in mixtures of sucrose and invert sugar, such as raw sugars, cane syrups and cane molasses, it is necessary to apply a correction when estimating the invert sugar in these by any method involving cupric reduction. Ling and Rendle (*ibid.* 33, 170) have determined the corrections to be applied for the influence of sucrose when their method is used for the analysis of mixtures such as those referred to.

In the following table:—

Column A gives the amounts in grams of sucrose present in 100 c.c. of the sugar solutions.

Column B gives the percentages of sucrose present expressed on the total sugars.

Column C gives the percentages of invert sugar present expressed on the total sugars.

Column D gives the number of cubic centimetres of sugar solution required to reduce 10 c.c. of Fehling's solution.

Column E gives the percentages of invert sugar on the total sugars found by direct experiment.

Column F gives the differences between the values shown in columns C and E.

In addition to these results Ling and Rendle (*l.c.*) also carried out determinations for mixtures of sucrose and invert sugar when the concentra-

tion of the latter sugar was 0.15 gm. and 0.25 gm. per 100 c.c. respectively.

TABLE XVI.

Each solution contained, in addition to the sucrose shown under column A, 0.2 gram of invert sugar per 100 c.c.

A	B	C	D	E	F
0.01	4.8	95.2	25.60	95.30	0.10
0.03	13.0	87.0	25.60	87.10	0.10
0.05	20.0	80.0	25.60	80.10	0.10
0.10	33.3	66.7	25.55	66.90	0.20
0.20	50.0	50.0	25.45	50.40	0.40
0.30	60.0	40.0	25.40	40.40	0.40
0.40	66.6	33.4	25.35	33.80	0.40
0.50	71.4	28.6	25.30	29.00	0.40
0.60	75.0	25.0	25.20	25.40	0.40
0.70	77.7	22.3	25.15	22.70	0.40
0.80	80.0	20.0	25.10	20.40	0.40
1.25	86.2	13.8	25.05	14.10	0.30
1.50	88.2	11.8	24.95	12.10	0.30
1.75	89.7	10.3	24.85	10.60	0.30
1.75	89.7	10.3	24.80	10.60	0.30
2.00	90.9	9.1	24.70	9.45	0.35
2.00	90.9	9.1	24.80	9.41	0.31
2.50	92.5	7.5	24.80	7.76	0.26
3.00	93.8	6.2	24.70	6.44	0.24
5.00	96.1	3.9	24.20	4.05	0.15
7.00	97.2	2.8	23.60	3.04	0.24
10.00	98.0	2.0	22.95	2.23	0.23
20.00	99.0	1.0	22.40	1.14	0.14
25.00	99.2	0.8	22.25	0.92	0.12
30.00	99.3	0.7	22.25	0.80	0.10

An examination of the table shows that the influence of sucrose is practically negligible until the proportion to the total sugars (sucrose and invert sugar) amounts to 30 p.c. (*see* column B), at which point the invert sugar is overestimated by 0.2 p.c. This influence of sucrose increases progressively until the proportion, expressed on the total sugars, 99.3 p.c. is reached, beyond which it has not been determined. At this point the invert sugar is overestimated to the extent of about 15 p.c. It must be remembered, however, that the magnitudes representing the percentages of invert sugar decrease as those representing the percentages of sucrose increase, and it will be seen that the correction to be applied (column F) is in concrete numbers the greatest when the percentage of sucrose on the total sugars is between 50 and 80. In the case of a mixture of equal parts of sucrose and invert sugar, the latter would be returned if no correction were applied as 50.4 p.c. instead of 50.0 p.c., whilst in the case of a mixture of 99 parts of sucrose and 1 part of invert sugar, the latter would be returned if no correction were applied as 1.14 p.c. instead of 1 p.c. The writer is in the habit in practice of deducting the values shown in column F of the table from the values determined by direct titration of the mixture of sugars. For this purpose, however, it is necessary to know the percentage of sucrose, not calculated on the sample, but on the total sugars (sucrose and invert sugar) in the sample. This can be determined either by the Clerget method or by the method of double titration before and after hydrolysis with hydrochloric acid, applying the formula $S = \frac{(95I' - I)}{100}$, in which S is the approximate percentage of sucrose,

I is the apparent percentage of invert sugar—*i.e.* the value obtained by direct titration—and I' is the percentage of invert sugar obtained by titration of the sample after complete hydrolysis.

The approximate value given in column F is subtracted from the value of I and added to the value of S, the respective results giving the corrected percentages of invert sugar and of sucrose. In order to express these on the sample, each of the values is multiplied by $S+I/100$. To be exact, the value added to the approximate percentage of sucrose, S, should be diminished by 5 p.c.; but the accuracy of the method does not warrant this refinement, seeing that the corrections to be applied are values of comparatively small magnitude.

J. H. Lane and L. Eynon (*J. Soc. Chem. Ind.* 1923, 42, 32 T) have recently proposed to use methylene blue as an indicator in titrating sugars with Fehling's solution. They add 3–5 drops of methylene blue to the Fehling's solution which they boil for 2 mins. with sufficient assay liquid so that not more than 1 c.c. of the latter is required to complete the reduction. They then boil with additional small quantities of the assay liquid for a further 1 min., the end point being complete decolorisation of the methylene blue.

Eynon and Lane (*J. Soc. Chem. Ind.* 1923, 42, 143 T) have shown that small amounts of calcium salts likely to be present with commercial sugar products vitiate the determination of reducing sugars seriously, the result being lower than the true value. For accurate determination of reducing sugars in such products it is recommended to decalcify the solution by means of potassium oxalate.

In the early days when the end point in the titration method was determined by the disappearance of the blue colour, a difficulty was experienced in titrating dark coloured physiological liquids with the ordinary Fehling's solution. Nor can the ferrocyanide indicator be used with these liquids, since they invariably contain amino compounds, which partially dissolve the precipitated cuprous oxide. It is true that cuprous solutions do not give a coloration with ferrocyanide, but it is necessary to acidify with acetic acid before this indicator can be applied, and acidified solutions of cuprous salts when exposed to air rapidly oxidise to the cupric state. The writer has not found the same difficulty with his ferrous thiocyanate indicator, which, in the absence of iron, may be used for the titration of physiological solutions.

To obviate the difficulties referred to in the preceding paragraph, F. W. Pavy, in 1879 (*Proc. Roy. Soc.* 28, 260), proposed to employ a copper solution containing sufficient ammonia to keep the reduced cuprous oxide in solution. Since the disturbing influence of the precipitated cuprous oxide on the colour is thus prevented as well as that due to the presence of amino compounds, it is possible, in absence of air, to titrate moderately dark-coloured physiological liquids, using Pavy's solution, with sufficient accuracy. The method has been applied specially for the estimation of dextrose in urine. It should be added, however, that the colour of many physiological liquids is sufficient to render accuracy impossible with Pavy's method.

Pavy's solution is prepared as follows:

crystallised copper sulphate (34.65 grms.), Rochelle salt (170 grms.) and potassium hydroxide (170 grms.) are dissolved in water and made up to one litre. The copper and alkaline tartrate solutions are preferably made up separately and equal volumes mixed as required (*see* p. 461). To 120 c.c. of the mixed solutions is added ammonia of sp.gr. 0.880 (300 c.c.), and the liquid is diluted to one litre. Working under the conditions to be described, 20 c.c. of this solution are reduced by 0.01 gm. of glucose. If other sugars are to be estimated, the titre of the solution must be established for each of these.

The titration is performed in the following manner. A round-bottomed flask of 150 c.c. capacity is provided with a doubly-bored rubber stopper. Through one opening in the stopper the delivery end of the burette passes and through the other a glass tube bent twice at right angles, the latter being intended for the escape of the steam and to prevent the access of air. Forty cubic centimetres of the ammoniacal copper solution are introduced into the flask and after inserting the stopper the solution is raised slowly to boiling. The assay liquid is then added at the rate of 60 to 100 drops per minute, ebullition being maintained meanwhile (a special pinch cock was employed by Pavy). When the blue colour is nearly discharged, the assay liquid is added drop by drop until no more blue can be discerned. A sheet of white paper or a plate of opal glass placed behind the flask assists in determining the end point more accurately.

For estimation of sugar in blood, *see* p. 484.

For the estimation of reducing sugars and sucrose, *see* Thomas and Dutcher (*J. Amer. Chem. Soc.* 1924, 46, 1662; *Analyst*, 1924, 49, 437).

For the estimation of reducing sugars in small quantities, Bang (*Biochem. Zeitsch.* 1906, 2, 271) makes use of the principle that cuprous oxide separates as cuprous thiocyanate from a solution of cupric sulphate containing alkali carbonates (not hydroxides) and potassium thiocyanate. The unreduced copper salt is then also precipitated as cuprous thiocyanate by titration with a standard solution of hydroxylamine in the presence of an excess of potassium thiocyanate. The method is said to be accurate and to be adapted for the estimation of sugar in urine. The following solutions are employed.

Copper solution.—Potassium carbonate (250 grms.), potassium bicarbonate (50 grms.) and potassium thiocyanate (211 grms.) are dissolved by warming in water (600 c.c.). To the cooled liquid is slowly added a solution of crystallised copper sulphate (12.5 grms.) in about 75 c.c. of water. The mixture is then made up to a litre.

Hydroxylamine solution.—Hydroxylamine sulphate (6.55 grms.) and potassium thiocyanate (200 grms.), are dissolved in water and the solution made up to two litres.

In carrying out the titration the sugar solution (10 c.c.), which should not contain more than 60 mgrms. of dextrose, is measured into a 200 c.c. flask and 50 c.c. of the copper solution added. The mixture is heated to boiling and maintained in ebullition for exactly 3 mins. The liquid is then cooled and the hydroxylamine solution run in from a burette until the blue

colour is completely discharged. The results are calculated by Table XVII.

TABLE XVII.

Hydroxyl-amine	Glucose	Hydroxyl-amine	Glucose
c c.	mgs.	c.c.	mgs.
43·85	5	17·75	33
42·75	6	16·95	34
41·65	7	16·15	35
40·60	8	15·35	36
39·50	9	14·60	37
38·40	10	13·80	38
37·40	11	13·05	39
36·40	12	12·30	40
35·40	13	11·50	41
34·40	14	10·90	42
33·40	15	10·20	43
32·45	16	9·50	44
31·50	17	8·80	45
30·55	18	8·20	46
29·60	19	7·65	47
28·65	20	7·05	48
27·75	21	6·50	49
26·85	22	5·90	50
26·00	23	5·35	51
25·10	24	4·75	52
24·20	25	4·20	53
23·40	26	3·60	54
22·60	27	3·05	55
21·75	28	2·60	56
21·00	29	2·15	57
20·15	30	1·65	58
19·35	31	1·20	59
18·55	32	0·75	60

Methods have been devised in which the cuprous oxide reduced under standard conditions by sugars is collected on a filter and subsequently dissolved and the copper titrated by one of the well-known methods. These will be referred to under gravimetric methods (see p. 467).

Gravimetric methods.—The preference shown by many workers for gravimetric methods as compared with volumetric methods is based on the fact that weighings can be conducted with a greater degree of delicacy than can titrations. But whilst this is true, it by no means follows that the former are less accurate than the latter. In the first place, the empirical character of methods depending on the reduction of cupric solutions by sugars must be borne in mind, for, even with solutions of pure sugars the variations of conditions in even a slight degree causes considerable alterations in the results, so that increased delicacy does not of necessity synchronise with increased accuracy. Moreover, in the case of commercial products there are other factors which tend to vitiate the accuracy of the gravimetric methods. Thus these products contain certain salts of the alkali earth metals and nitrogenous matters. The former are liable to be precipitated with the cuprous oxide, whilst the latter are capable of dissolving some of the cuprous oxide. Errors of the former kind may be avoided by dissolving the washed cuprous oxide and estimating the copper volumetrically ; but it is impossible to eliminate the errors due

to the solvent action of the nitrogenous matters on the cuprous oxide. Neither of these factors affects the accuracy of methods of direct titration. Concordance of results in gravimetric methods does not, therefore, of necessity indicate accuracy.

It is impossible in this article to deal exhaustively with the numerous methods which have been proposed for the estimation of reducing sugars by weighing the cuprous oxide precipitated under standard conditions. The writer must confine himself to a description in detail of some of those methods which are in most general use. Taking them in their chronological order, the principal investigators to whom we are indebted for our knowledge on this subject are Soxhlet, Allihn, Wein, Meissl, Herzfeld, Lehmann, Kjeldahl, Brown, Morris and Millar, Defren, and Bertrand.

In most of the new methods, workers have started on an entirely new basis from that adopted by those that preceded them, altering not only the composition of the alkaline copper solution but also the mode of carrying out the reduction. Thus some use a larger proportion of alkali, whilst others have departed from the original prescription of Fehling so far as to employ potassium hydroxide instead of sodium hydroxide.¹ It therefore happens that we are in possession of a large number of empirical tables which can only be used under strictly standardised conditions.

In the earlier gravimetric methods the cuprous oxide was collected on a paper filter, and after washing, the precipitate and filter were ignited and the copper weighed as cupric oxide. This method is subject to several errors, *e.g.* the paper in spite of repeated washing retains some of the copper, possibly by adsorption, and as this is by no means a constant quantity it cannot be corrected for ; again, it is difficult to burn the precipitate to cupric oxide in a crucible even if, after one burning, it be treated with nitric acid and again ignited. The method has, therefore, now been superseded by one in which the cuprous oxide is collected under diminished pressure in a Soxhlet tube packed with asbestos. The following is a description of a Soxhlet tube. The tube is made of hard glass, and the total length is about 20 cms. The upper portion is a parallel-walled tube, having an internal diameter of about 1·5 cms., and is about 12 cms. long. Below this the tube is constricted to a bore of about 1 mm., and the remaining portion of the tube below the constriction tapers towards the end in order that it may be fitted into the hole of a rubber stopper which fits into the filter flask attached to the pump. The Soxhlet tube is packed with asbestos in the manner to be described. Another method of collecting the cuprous oxide obtained by the reduction of Fehling's solution is by the use of a Gooch crucible, which is also packed with asbestos.

The asbestos used for this purpose must be subjected to treatment with acid and alkali, otherwise it loses weight when the alkaline

¹ In this connection it should be pointed out that Glendinning (Chem. Soc. Trans. 67, 999) has shown that, other things being equal, considerably higher results are obtained when potassium hydroxide is substituted for the sodium compound.

copper solution is filtered through it. The following method recommended for this purpose by Munson and Walker (J. Amer. Chem. Soc. 28, 666) may be used. The asbestos, which should be of the amphibole variety, is digested with 1:3 hydrochloric acid for 2 to 3 days, after which it is washed free from acid and digested for a similar period with soda solution,¹ following which it is treated with hot Fehling's solution. The asbestos is now washed free from alkali and finally digested with nitric acid for several hours, after which it is washed free from acid and suspended in water for use. It is best kept suspended in water in a wide-mouthed stoppered bottle.

To prepare a Soxhlet tube for use, a small amount of the prepared asbestos suspended in water is introduced into the tube which is in connection with the filter pump, just as it would be when being used for the collection of the copper precipitate. The tube thus charged with asbestos is then dried in the water oven and cooled in the desiccator when it is ready for use.

A Soxhlet tube, prepared as just described, is tared, and the cuprous oxide having been collected in it and washed with hot water, principally by decantation, the tube is dried in the water oven. The drying may be facilitated by washing finally with alcohol and ether before placing in the oven. The most commonly adopted plan is to reduce the cuprous oxide to metallic copper before weighing. This is done by connecting the wider end of the tube with a hydrogen generating apparatus and igniting that portion of the tube containing the cuprous oxide by a Bunsen flame, a current of hydrogen being passed through the tube meanwhile. Prior to this, however, in the most exact work, especially with commercial products, it is advisable to ignite in a current of oxygen in order to remove any organic matter that may have been precipitated with the cuprous oxide. Some chemists weigh the precipitate as cupric oxide after ignition in a current of oxygen. It has also been proposed to weigh the precipitate after merely drying, and in the case of sugar solutions not containing other organic matters this appears not to be attended with any error (*cf.* O'Sullivan and Stern, Chem. Soc. Trans. 69, 1691). Ling and Davis (J. Inst. Brewing, 8, 477), employing a Gooch crucible, weighed the copper precipitate as cuprous oxide, that is to say, they merely dried it after collection, and their results show that with pure solutions this procedure is justifiable on the score of accuracy. Whichever method is adopted, the Soxhlet tube or Gooch crucible, after being weighed with the copper, should be treated with nitric acid to dissolve the copper, and the asbestos thoroughly washed. After drying, the tare of the tube should be the same as it was at the commencement of the experiment.

The washed cuprous oxide collected on a Soxhlet tube or Gooch crucible may also be dissolved in nitric acid or a mixture of that acid and sulphuric acid, the copper deposited electrolytically and weighed as metal (see Bull. 107 [revised], U.S. Bur. of Chem. p. 49). Peters has devised a rapid electrolytic method of

estimating copper (J. Amer. Chem. Soc. 34, 426). Another electrolytic method is that of Sand described in the Report of the British Association for the Advancement of Science, 1910.

The washed cuprous oxide may be dissolved in a solution of ferric sulphate containing sulphuric acid and the ferrous salt produced titrated with permanganate. Many modifications of this process have been proposed. The latest and best known is that of Bertrand (*see* p. 468). A further modification is described in Bull. 107, U.S. Bur. of Chem. *l.c.* In this, the strength of the permanganate used is $N/20$.

Another method of estimating the cuprous oxide reduced by sugar solutions is based on the well-known principle of liberation of iodine by cupric salts and titration of the iodine with thiosulphate. The washed precipitate is dissolved in nitric acid, and the solution boiled until the red fumes are expelled. It is then made alkaline with ammonia and acidified with acetic acid. An excess of potassium iodide is then added and the liberated iodine is titrated in the well-known manner (Low, J. Amer. Chem. Soc. 24, 1082; Kendall, *ibid.* 23, 1947; Peters, *ibid.* 34, 422). This iodometric method gives low results as compared with those obtained by the gravimetric method (Sherwood and Wiley, Bull. 105, U.S. Bur. of Chem. p. 120).

Iodimetric estimation of sugars.—It has been shown by Willstätter and Schüdel (Ber. 1918, 51, 780); H. M. Judd (Bio-Chem. J. 1920, 14, 255); Baker and Hulton (*ibid.* 754); and Cajori (J. Biol. Chem. 1922, 54, 617), that iodine oxidises aldoses quantitatively to the corresponding mono-carboxylic acids, whilst ketoses are practically unaffected. The method however, yields results which vary according to conditions. The most recent paper on the subject is that of C. L. Hinton and T. Macara (Analyst, 1924, 48, 2), who show the effects of varying the concentration of the sugar solution, the amount and nature of the alkali used, the amount of iodine used, and the time and temperature during and at which the reaction is allowed to proceed. The iodine equivalents of dextrose, lactose, sucrose, lævulose, and invert sugar obtained by a standard procedure are given. The method adopted consists in adding to 50 c.c. of the sugar solution containing about 0.08 gm. of dextrose or its equivalent, 40 c.c. of 0.05 *N*-iodine, and 5 c.c. of 0.5 *N*-sodium hydroxide solution. After the mixture has been kept at 17.5°C. for 10 minutes, 5 c.c. of 2*N*-sulphuric acid are run in and the excess of iodine is titrated with 0.05 *N*-sodium thiosulphate solution. Under these conditions dextrose and lactose are quantitatively oxidised to monobasic acids, whilst sucrose and lævulose are but slightly acted upon but yield constant results if the above conditions are observed. The weight of iodine combining with 1 gm. of the sugars investigated is for dextrose 1.410, lactose hydrate 0.705, sucrose 0.003, lævulose (in large amount) 0.0065, lævulose (in presence of an equal weight of dextrose) 0.012, and invert sugar 0.710 gm. The estimation of sucrose may be carried out by an iodine titration before and after inversion if the inversion is conducted at temperatures below 60°C. The iodine value of sucrose is then 0.774 for the difference

¹ The writer uses a 50 p.c. solution of sodium hydroxide for this purpose.

between ‘direct’ and ‘invert’ estimations. The quantitative conversion of sucrose to invert sugar is impossible when the solution is boiled with acid, but by using 0.284 p.c. by weight of hydrochloric acid in the solution and heating for 10 minutes at 60°C. satisfactory results are obtained. For technical purposes invert sugar may be estimated in many products by a single titration with iodine, and no difficulty is encountered in its estimation in jams or commercial invert sugars. The use of weaker alkalis, such as sodium carbonate or borax instead of sodium hydroxide, was investigated, but no advantage was found, and a longer reaction time or a higher temperature was necessitated by their use (J. Inst. Brewing, 1920, 26, 426 ; 1921, 27, 189 ; J. Soc. Chem. Ind. 1914, 33, 948 ; J. Inst. Brewing, 1924, 30, 232).

For the isolation of sucrose from mixtures of dextrose lævulose, and sucrose, see Komatsu and Tanimura (Mem. Coll. Sci. Kyoto, 1924, 7, 161 ; Chem. Soc. Abstr. 1924. 126, i. 13).

Allihn’s method.—One of the best known and most widely used methods of estimating dextrose gravimetrically by the cupric reduction method is that of Allihn (J. prakt. Chem. [ii.], 22, 46), but it has not been applied to any other sugar. The copper reagent used has the following composition :—

Solution I.—Crystallised copper sulphate (34.6 grms.) is dissolved in water and the solution made up to 500 c.c.

Solution II.—Rochelle salt (173 grms.) and potassium hydroxide (125 grms.) are dissolved in water and the solution made up to 500 c.c.

Equal volumes of 30 c.c. of each of the two solutions are measured out into a beaker and diluted with 60 c.c. of water. A volume of 25 c.c. of a standard solution of the sample to be examined, which must not contain more than 0.25 gm. of dextrose, is added and the solution is raised to the boiling-point, ebullition being continued for 2 mins. It is important in this and in all other estimations of the kind that the beaker should be covered with a clock glass during the ebullition.¹ The cuprous oxide is collected at once in a Soxhlet tube, washed, dried, and reduced in a current of hydrogen in the manner already described. In Table XVIII., which is an abridged form of that given for the Allihn method by the A. O. A. C. (Bull. 107 [revised], U.S. Bur. of Chem., p. 49), the weight of copper and of cuprous oxide corresponding to different weights of dextrose are given.

¹ The reason that it is necessary to cover the beaker with a clock glass has already been alluded to as well as the observations of Kjeldahl (*l.c.*) on this point. Kjeldahl went even further and suggested carrying out the reduction in a flask immersed in a bath of boiling water, a current of hydrogen being passed through the solution during the ebullition. Kjeldahl’s method has been modified by Woy (Zeits. öffentl. Chem. 6, 514 ; 519). Working with pure sugar solutions there is no doubt that more concordant results can be obtained in this way, but with commercial products, in which this atmospheric oxidation is perhaps one of the least factors which conduce to error, the covering of the beaker with a clock glass is a sufficient precaution to guard against atmospheric oxidation. In the Allihn method the size of the beaker, the kind and height of the flame employed also influence the results. On this account the O’Sullivan method of heating in a boiling water bath as adopted by Kjeldahl, Brown, Morris and Millar (see this page), and others is to be preferred.

TABLE XVIII.—*Allihn’s Table for Estimating Dextrose.*

Copper (Cu)	Cuprous oxide (Cu ₂ O)	Glucose	Copper (Cu)	Cuprous oxide (Cu ₂ O)	Glucose
mgs.	mgs.	mgs.	mgs.	mgs.	mgs.
11	12.4	6.6	241	271.3	124.4
16	18.0	9.0	246	277.0	127.1
21	23.6	11.5	251	282.6	129.7
26	29.3	14.0	256	288.2	132.4
31	34.9	16.5	261	293.8	135.1
36	40.5	18.9	266	299.5	137.8
41	46.2	21.4	271	305.1	140.6
46	51.8	23.9	276	310.7	143.3
51	57.4	26.4	281	316.4	146.1
56	63.0	28.8	286	322.0	148.8
61	68.7	31.3	291	327.4	151.6
66	74.3	33.3	296	333.3	154.3
71	79.9	36.3	301	338.9	157.1
76	85.6	38.8	306	344.5	159.8
81	91.2	41.3	311	350.1	162.6
86	96.8	43.9	316	355.8	165.3
91	102.4	46.4	321	361.4	168.1
96	108.1	48.9	326	367.0	170.9
101	113.7	51.4	331	372.7	173.7
106	119.3	54.0	336	378.3	176.5
111	125.0	56.5	341	383.9	179.3
116	130.6	59.1	346	389.6	182.1
121	136.2	61.6	351	395.2	184.9
126	141.9	64.2	356	400.8	187.7
131	147.5	66.7	361	406.4	190.6
136	153.1	69.3	366	412.1	193.4
141	158.7	71.8	371	417.7	196.3
146	164.4	74.4	376	423.3	199.1
151	170.0	77.0	381	429.0	202.0
156	175.6	79.6	386	434.6	204.8
161	181.3	82.2	391	440.2	207.7
166	186.9	84.8	396	445.9	210.6
171	192.5	87.4	401	451.5	213.5
176	198.1	90.0	406	457.1	216.4
181	203.8	92.6	411	462.7	219.3
186	209.4	95.2	416	468.4	222.2
191	215.0	97.8	421	474.0	225.1
196	220.7	100.5	426	479.6	228.0
201	226.3	103.1	431	485.3	231.0
206	231.9	105.8	436	490.9	233.9
211	237.6	108.4	441	496.5	236.9
216	243.2	111.1	446	502.1	239.8
221	248.7	113.7	451	507.8	242.8
226	254.4	116.4	456	513.4	245.7
231	260.1	119.0	461	519.0	248.7
236	265.7	121.7			

Meissl’s method for the estimation of invert sugar (Zeit. Ver. Deut. Zuckerind, 29, 1050) is carried out in the same manner as Allihn’s dextrose method, but the copper solution employed was that of Soxhlet, containing 52 grms. per litre of sodium hydroxide. Wein (Tabellen für quantitative Bestimmung der Zuckerarten, 1888) used the same solution for the estimation of maltose and other sugars. The results for maltose calculated by Wein’s tables were found to be 5 p.c. too low by Brown, Morris and Millar (Chem. Soc. Trans. 71, 105), and this has been confirmed by Ling and Baker (*ibid.* 509).

Standard gravimetric methods have been devised, each of which is capable of being used

for the estimation of several sugars. The first of these which will be described here is that of Brown, Morris and Millar (*l.c.*) for the estimation of dextrose, lævulose, invert sugar and maltose. The method adopted is that of O'Sullivan. The copper reagent employed had the following composition. Crystallised copper sulphate (34.6 grms.), Rochelle salt (173 grms.), sodium hydroxide (65 grms.), and water to one litre.¹

Fifty cubic centimetres of the copper solution are introduced into a beaker, the surface area of which is 44 sq. cms. The beaker is covered with a clock glass and immersed in a bath of boiling water. When the solution has attained the same temperature as that of the bath, the sugar solution is added and the mixture made up to approximately 100 c.c. with boiling water and heated in the boiling water bath for exactly 12 mins. The amount of sugar employed must be that which will give a weight of cupric oxide lying within the limits of 0.15 to 0.35 gm. The filtration is performed as rapidly as possible through a Soxhlet's tube under reduced pressure, and the cuprous oxide is either oxidised to cupric oxide in a current of oxygen or reduced to copper in a current of hydrogen. The results are calculated by Tables XIX.-XXII.

Defren (*J. Amer. Chem. Soc.* 18, 751) has

TABLE XIX.—*Dextrose.*

Dextrose mgrms.	Cu weighed grms.	CuO weighed grms.	Cu corresponding to 1 gm dextrose	CuO corresponding to 1 gm. dextrose
50	0.1030	0.1289	2.060	2.578
55	0.1134	0.1422	2.066	2.585
60	0.1238	0.1552	2.068	2.587
65	0.1342	0.1682	2.069	2.589
70	0.1443	0.1809	2.066	2.585
75	0.1543	0.1935	2.062	2.580
80	0.1644	0.2061	2.059	2.577
85	0.1740	0.2187	2.055	2.572
90	0.1834	0.2299	2.042	2.555
95	0.1930	0.2420	2.036	2.547
100	0.2027	0.2538	2.029	2.538
105	0.2123	0.2662	2.027	2.535
110	0.2218	0.2781	2.021	2.528
115	0.2313	0.2900	2.016	2.522
120	0.2404	0.3014	2.008	2.512
125	0.2496	0.3130	2.002	2.504
130	0.2585	0.3241	1.993	2.493
135	0.2675	0.3354	1.986	2.484
140	0.2762	0.3463	1.977	2.473
145	0.2850	0.3573	1.970	2.464
150	0.2934	0.3673	1.957	2.448
155	0.3020	0.3787	1.953	2.443
160	0.3103	0.3891	1.944	2.432
165	0.3187	0.3996	1.936	2.422
170	0.3268	0.4098	1.926	2.410
175	0.3350	0.4200	1.918	2.400
180	0.3431	0.4302	1.910	2.390
185	0.3508	0.4399	1.900	2.377
190	0.3590	0.4501	1.894	2.369
195	0.3668	0.4599	1.885	2.358
200	0.3745	0.4689	1.874	2.344
205	0.3822	0.4792	1.869	2.338

worked out a method for the estimation of dextrose, maltose and lactose. He employs, like Meissl and Wein (see above), Soxhlet's formula for Fehling's solution, but he adopts the O'Sullivan method.

TABLE XX.—*Lævulose.*

Lævu-lose mgrms.	Cu weighed grms.	CuO weighed grms.	Cu corresponding to 1 gm. lævulose	CuO corresponding to 1 gm. lævulose
50	0.0923	0.1155	1.847	2.310
55	0.1027	0.1287	1.856	2.341
60	0.1122	0.1407	1.859	2.345
65	0.1216	0.1524	1.860	2.346
70	0.1312	0.1645	1.863	2.350
75	0.1405	0.1761	1.862	2.349
80	0.1500	0.1881	1.864	2.351
85	0.1590	0.1993	1.859	2.345
90	0.1686	0.2114	1.862	2.349
95	0.1774	0.2224	1.856	2.341
100	0.1862	0.2331	1.848	2.331
105	0.1952	0.2447	1.848	2.331
110	0.2040	0.2558	1.843	2.325
115	0.2129	0.2669	1.840	2.321
120	0.2215	0.2777	1.834	2.314
125	0.2303	0.2887	1.831	2.310
130	0.2390	0.2997	1.827	2.305
135	0.2477	0.3106	1.823	2.300
140	0.2559	0.3209	1.817	2.292
145	0.2641	0.3311	1.811	2.284
150	0.2723	0.3409	1.802	2.273
155	0.2805	0.3517	1.709	2.269
160	0.2889	0.3622	1.795	2.264
165	0.2972	0.3726	1.790	2.258
170	0.3053	0.3828	1.785	2.252
175	0.3134	0.3930	1.779	2.245
180	0.3216	0.4032	1.775	2.240
185	0.3297	0.4134	1.770	2.234
190	0.3377	0.4234	1.765	2.228
195	0.3457	0.4335	1.761	2.223
200	0.3539	0.4431	1.755	2.216
205	0.3616	0.4534	1.751	2.211

Bertrand (*Bull. Soc. chim.* [iii.] 35, 1285) has elaborated a method for the estimation of invert sugar, dextrose, galactose, maltose and lactose. His reagent has the following composition:

Solution I.—Crystallised copper sulphate (40 grms.) is dissolved in water and made up to one litre.

Solution II.—Rochelle salt (150 grms.) and sodium hydroxide (150 grms.) are dissolved in water and made up to one litre.

His method is carried out as follows: A sugar solution (20 c.c.) which should not contain more than 0.1 gm. of reducing sugars is transferred to a 150 c.c. Erlenmeyer flask, and 20 c.c. of each of the two solutions forming the copper reagent added. The mixture is then heated to boiling, and maintained in gentle ebullition for exactly 3 mins. The liquid is then filtered through a Gooch crucible, or a special tube packed with asbestos, the precipitate washed as usual and the reduced copper estimated volumetrically by the permanganate method (see p. 466). Table XXIII. is Bertrand's table abridged from the original.

¹ The copper sulphate solution and the alkaline Rochelle salt solution are, of course, kept separate.

TABLE XXI.—*Invert Sugar.*

Invert sugar mgrms.	Cu weighed grms.	CuO weighed grms.	Cu corre- sponding to 1 grm. invert sugar	CuO corre- sponding to 1 grm. invert sugar
50	0·0975	0·1221	1·952	2·442
55	0·1076	0·1349	1·961	2·453
60	0·1176	0·1474	1·964	2·457
65	0·1275	0·1598	1·966	2·459
70	0·1373	0·1721	1·966	2·459
75	0·1468	0·1840	1·962	2·454
80	0·1566	0·1963	1·962	2·454
85	0·1662	0·2084	1·960	2·451
90	0·1755	0·2200	1·955	2·445
95	0·1848	0·2317	1·950	2·439
100	0·1941	0·2430	1·943	2·430
105	0·2034	0·2550	1·942	2·429
110	0·2128	0·2668	1·939	2·425
115	0·2220	0·2783	1·935	2·420
120	0·2311	0·2898	1·931	2·415
125	0·2400	0·3009	1·925	2·407
130	0·2489	0·3121	1·920	2·400
135	0·2578	0·3232	1·915	2·394
140	0·2663	0·3339	1·908	2·385
145	0·2750	0·3448	1·902	2·378
150	0·2832	0·3546	1·891	2·364
155	0·2915	0·3655	1·886	2·358
160	0·3002	0·3764	1·881	2·352
165	0·3086	0·3869	1·875	2·345
170	0·3167	0·3971	1·868	2·336
175	0·3251	0·4076	1·862	2·329
180	0·3331	0·4177	1·855	2·320
185	0·3410	0·4276	1·848	2·311
190	0·3490	0·4376	1·842	2·303
195	0·3570	0·4476	1·836	2·295
200	0·3650	0·4570	1·828	2·285
205	0·3726	0·4672	1·823	2·279

As already mentioned, numerous other metallic solutions besides that originally devised by Fehling have been used for the detection and estimation of reducing sugars. These will now be dealt with in outline.

Barfoed (Zeitsch. anal. Chem. 12, 27) proposed to use a solution one part of crystallised neutral copper acetate in 15 parts of water. To 200 c.c. of this solution are added 5 c.c. of 38 p.c. acetic acid before use. Barfoed's solution is not reduced to any great extent by the bioses maltose, lactose, &c., but although it has some value in the case of mixture of monoses and bioses, this applies to it for qualitative rather than quantitative purposes.

It has been proposed by Soldaini (Ber. 9, 1126) and also subsequently by another chemist of the same name (Zeits. Ver. Deut. Zuckerind. 39, 933 ; 40, 792) to employ a copper bicarbonate solution for the estimation of reducing sugars. The disadvantages of such a solution, however, outweigh its advantages, since there is always the possibility of the precipitation of cupric hydroxide, in addition to which calcium and other salts which are present in commercial products, are precipitated with the cuprous oxide. More recently Ost has suggested a modification of the Soldaini reagent (Chem. Zeit. 19, 1784, 1829).

Before dismissing copper methods, attention

may be called to a paper by Kendall (J. Amer. Chem. Soc. 34, 317). Fehling's solution prepared with Rochelle salt is well known to be liable to spontaneous reduction, especially if the copper and Rochelle salt solutions have been kept mixed for some time. Kendall tried various other salts to replace the Rochelle salt, and finally came to the conclusion that a cupric solution containing an alkali carbonate and salicylate remained perfectly stable in absence of extraneous reducing substances. The method adopted is as follows : An appropriate volume of the sugar solution is measured out into a 200 c.c.

TABLE XXII.—*Reducing Values of Varying Quantities of Maltose under Standard Conditions.*

Maltose mgrms.	Cu weighed grms.	CuO weighed grms.	Cu corre- sponding to 1 grm. maltose	CuO corre- sponding to 1 grm. maltose
70	0·0772	0·0966	1·1029	1·3800
75	0·0826	0·1034	1·1026	1·3796
80	0·0880	0·1102	1·1023	1·3792
85	0·0934	0·1169	1·1020	1·3788
90	0·0988	0·1237	1·1017	1·3784
95	0·1042	0·1305	1·1013	1·3780
100	0·1097	0·1373	1·1010	1·3777
105	0·1151	0·1441	1·1007	1·3773
110	0·1205	0·1509	1·1004	1·3769
115	0·1259	0·1576	1·1001	1·3765
120	0·1313	0·1644	1·0997	1·3761
125	0·1367	0·1712	1·0994	1·3757
130	0·1422	0·1779	1·0991	1·3754
135	0·1476	0·1848	1·0988	1·3750
140	0·1530	0·1916	1·0985	1·3746
145	0·1584	0·1983	1·0981	1·3742
150	0·1634	0·2051	1·0978	1·3738
155	0·1692	0·2119	1·0975	1·3734
160	0·1747	0·2186	1·0972	1·3731
165	0·1801	0·2254	1·0969	1·3727
170	0·1855	0·2323	1·0965	1·3723
175	0·1909	0·2490	1·0962	1·3719
180	0·1963	0·2458	1·0959	1·3715
185	0·2017	0·2526	1·0956	1·3711
190	0·2072	0·2593	1·0953	1·3703
195	0·2126	0·2661	1·0949	1·3704
200	0·2180	0·2729	1·0946	1·3700
205	0·2234	0·2797	1·0943	1·3696
210	0·2288	0·2865	1·0940	1·3692
215	0·2342	0·2933	1·0937	1·3688
220	0·2397	0·3000	1·0933	1·3685
225	0·2451	0·3068	1·0930	1·3681
230	0·2505	0·3136	1·0927	1·3677
235	0·2559	0·3203	1·0924	1·3673
240	0·2613	0·3272	1·0921	1·3669
245	0·2667	0·3340	1·0917	1·3665
250	0·2722	0·3407	1·0914	1·3662
255	0·2776	0·3475	1·0911	1·3658
260	0·2830	0·3543	1·0908	1·3654
265	0·2884	0·3610	1·0905	1·3650
270	0·2938	0·3678	1·0901	1·3646
275	0·2992	0·3747	1·0898	1·3642
280	0·3047	0·3814	1·0895	1·3639
285	0·3101	0·3882	1·0892	1·3635
290	0·3155	0·3950	1·0889	1·3631
295	0·3209	0·4017	1·0885	1·3627
300	0·3264	0·4085	1·0882	1·3623
305	0·3318	0·4154	1·0879	1·3619

TABLE XXIII.—*Bertrand's Table for Estimating Invert Sugar, Glucose, Galactose, Maltose, and Lactose.*

Milli-grams of sugar	Milligrams of copper corresponding to				
	Invert sugar	Glucose	Galac-tose	Maltose	Lactose
10	20·6	20·4	19·3	11·2	14·4
15	30·5	30·2	28·6	16·7	21·4
20	40·4	40·1	37·9	22·2	28·4
25	49·8	49·6	47·0	27·7	35·2
30	59·3	59·1	56·2	33·3	42·1
35	68·5	68·3	65·0	38·7	48·7
40	77·7	77·5	73·9	44·1	55·4
45	86·5	86·4	82·5	49·5	61·9
50	95·4	95·4	91·2	55·0	68·5
55	104·0	104·1	99·7	60·3	74·9
60	112·6	112·8	108·3	65·7	81·4
65	120·9	121·3	116·6	71·1	87·7
70	129·2	129·8	125·0	76·5	94·1
75	137·2	137·9	133·1	81·8	100·4
80	145·3	146·1	141·3	87·2	106·7
85	153·2	154·0	149·4	92·6	112·9
90	161·1	162·0	157·6	98·0	119·1
95	168·8	169·9	165·6	103·2	125·2
100	176·5	177·8	173·6	108·4	131·4

Erlenmeyer flask and the volume made up to 100 c.c. Five grams of salicylic acid are added, 15 c.c. of copper sulphate solution (containing 2 grms. of crystallised copper sulphate) and 25 c.c. of potassium carbonate solution (containing 15 grms. of the carbonate). This order must be adhered to and the mixture must not be agitated until all the constituents have been introduced, when the flask is rotated, and as soon as all the salicylic acid is dissolved the flask is placed in a boiling water bath for 20 mins. The cuprous oxide is then collected on an asbestos filter, washed and the copper estimated iodometrically by a modification devised by Kendall (*ibid.* 33, 1947). H. Yessen-Hansen (Compt. rend. Carlsberg, 1923, 15, No. 3; J. Soc. Chem. Ind. 1923, 1237 A) has devised a gravimetric method for estimating invert sugar or lactose in presence of sucrose.

Knapp's alkaline mercuric cyanide solution (Zeitsch. anal. Chem. 9, 395).—This reagent is prepared by dissolving mercuric cyanide (10 grms.) in 100 c.c. of sodium hydroxide solution of sp.gr. 1·145, and making up the solution to one litre. A measured volume of the reagent is heated to boiling and the sugar solution added from a burette until a drop of the filtered solution shows when acidified with acetic acid no coloration with ammonium sulphide. The final

point is by no means sharp and the method is but little used at the present time.

Sachsse's alkaline mercuric iodide solution (Zeits. Ver. Deut. Zuckerind. 26, 872).—To prepare this solution, mercuric iodide (18 grms.)—mercuric chloride is precipitated with potassium iodide, the precipitate washed and dried at 100° —is dissolved in a solution containing 80 grms. of potassium hydroxide. The solution is then made up to one litre. A solution of stannous chloride containing an excess of potassium hydroxide is used for determining the final point.

Composition of commercial sugars.—It may be pointed out that the values given under 'Polarisation' are those obtained by reading normal (Ventzke) solutions, clarified with the minimum quantity of basic lead acetate solution, in a 2-dm. tube. It will be observed that in the case of beet products the reducing sugars which are calculated as invert sugar are given as a trace. This means that the quantity present was less than 0·05 p.c. In the case of stored beet products, however, it frequently happens that from 0·5 to 5·0 p.c. and even more of reducing sugars are present, their production being due to the action of certain bacteria on the sucrose.

Raw beet products.—The direct polarisation of beet products as a rule gives a value closely approximating the true percentage of sucrose, an exception to this being when raffinose is present. In products containing raffinose, the direct polarisation must of necessity be in excess of the true percentage of sucrose, since the specific rotatory power of raffinose is greater than that of sucrose.

The composition of normal beet products of different grade is as follows:—

Beet crystals.—This product contains 99·8–99·9 p.c. of sucrose with 0·05 to 0·07 p.c. of ash. It is obtained in the beet factory by steam washing the first massecuite in a centrifugal machine.

The raw beet sugars which go to the refiner have the average composition shown below. The so-called 'rendement' or refinery yield is obtained by deducting five times the ash from the polarisation or sucrose percentage. This method of determining the refinery yield was first suggested by Scheibler, and was based on the fact that beet molasses¹ in his time contained on an average 50 p.c. of sucrose and 10 p.c. of ash (see below). He therefore assumed that the mineral matter in raw sugars prevented five times its weight of sugar from crystallising. It is now known that the so-called other organic matters, especially those which are colloidal, have a far greater melassigenic effect than the mineral matters, *per se*.

Raw Beet Products.

	I		II		III	
	First runnings		Second runnings		After-products	
Polarisation	96·0	95·5	93·5	91·0	90·0	85·5
Reducing sugars	trace	trace	trace	trace	trace	trace
Ash	0·8	1·2	1·7	2·5	3·0	4·8
Water	1·7	1·7	2·5	3·5	3·5	4·2
Other organic matter	1·5	1·6	2·3	3·0	3·5	5·5
	100·0	100·0	100·0	100·0	100·0	100·0

¹ Molasses is the final product in the manufacture of sugar. Although containing sugar, this cannot be separated from it by direct crystallisation.

Molasses.

Polarisation	50.0
Reducing sugars	trace
Ash	10.0
Water	20.0
Other organic matter	20.0
	<hr/>
	100.0

Raw products are also met with intermediate in composition between the three grades of solid sugars above referred to. So perfect are the systems now employed in the extraction of sugar from beet that the sucrose content of the molasses is often as low as 46 p.c. It has been mentioned already that beet products are liable to contain raffinose (see this vol. p. 460). Since this sugar is more soluble than sucrose, and as it is present in small amount, it necessarily accumulates in the molasses. Hence those products which are recovered from molasses are more likely to contain raffinose.¹ In some samples of beet molasses, as much as 15 p.c. of raffinose has been found by the optical method. It will have been noticed that in normal beet products the other organic matters are invariably in excess of the ash. When this is not the case, the presence of raffinose is to be suspected.

	Java basket sugar	
Polarisation	98.0	96.0
Reducing sugar	0.5	1.3
Ash	0.3	0.6
Water	0.2	1.0
Other organic matter	0.5	1.1
	<hr/>	<hr/>
	100.0	100.0

Low, dark-coloured solid cane products are met with in commerce under the following descriptions: Madras Jaggery, Java Stoopes, Panela, Penang, Brazilian syrups, Mauritius syrups and Egyptian. The quantity of these low products imported into this country is much less than in former times, since with improved machinery and methods a larger proportion of high-grade products is now turned out at the different cane factories all over the world. On this account also such as are imported are much less pure than formerly. The average analytical values obtained with these low products are within the following limits:—

Polarisation	85 to 60 p.c.
Invert sugar	10 to 15 „
Soluble ash	3 to 6 „

The values given under ‘Polarisation’ in the case of raw cane sugars are always less than the sucrose percentages determined by the Clerget method, since these products invariably

¹ The fact that raffinose is found in the largest quantity in sugars recovered from molasses by one of the alkali earth processes led chemists to believe that this sugar was formed by the action of the alkali earths; but von Lippmann has shown that raffinose is present in beet juice (Annalen, 232, 169). However, raffinose contains a galactose residue, and bearing in mind Lobry de Bruyn’s discovery of the reciprocal conversion of dextrose, lævulose and galactose under the action of alkalis, the possibility is by no means excluded that galactose may be formed by the action of the alkali earths on dextrose and lævulose in the sugar works and that this galactose may condense with sucrose forming raffinose.

Raw beet sugars containing raffinose—and these are most frequently molasses recovery products or low after products—are, as a rule, fine grained and woolly in appearance.

The following are some analyses of raw beet sugars containing raffinose ²:—

	I.	II.
Polarisation	92.1	89.4
Sucrose	91.0	86.8
Raffinose	0.6	1.4
Reducing sugar	trace	trace
Ash	1.7	2.1
Water	3.5	5.0
Other organic matter	3.2	4.7
	<hr/>	<hr/>
	100.0	100.0

In certain rare cases, 3 p.c. of raffinose and more has been found in sugars recovered from molasses.

For the estimation of raffinose in sugars, see Saillard (Compt. rend. 1924, 178, 2189; Analyst, 1924, 49, 437).

Raw cane products.—These are subject to a much greater variation in composition than are raw beet products. A few typical examples only will be given.

Cuban centrifugal sugar		Cuban molasses sugar	
97.0	96.50	86.5	80.5
1.0	1.30	2.2	4.5
0.5	0.55	2.7	3.5
0.5	0.60	4.2	3.0
1.0	1.05	4.4	8.5
<hr/>	<hr/>	<hr/>	<hr/>
100.0	100.00	100.0	100.0

contain reducing sugars which are more or less lævo-rotatory. The polarisations cannot, however, be corrected for these reducing sugars, as their rotatory constants are not always those of invert sugar.

Many raw cane sugars are sold for direct consumption, but the most popular types of these are Demerara sugars and cane products resembling them. These sugars polarise from 95–98 p.c. and contain from 1.5 to 0.5 p.c. of reducing sugar and from 1.5 to 1.0 p.c. of moisture. Occasionally the percentage of reducing sugars is higher. This is likely to be the case with products which have been stored. Products of like appearance to these types of sugar, which consist however of dyed beet sugar, have for some time been on the market. The dyes employed for the purpose are brilliant yellow S, an azo dye, and phosphine. The former gives a fine violet red colour with acids, whilst the latter remains unchanged on addition of acids. It may be detected, however, by dissolving the suspected sugar in water, rendering the solution alkaline and shaking it with ether, when a yellow-coloured ethereal extract, having a greenish fluorescence, is obtained. It should be pointed out that cane products as well as beet are now dyed in the manner described, and in some cases colouring with molasses is resorted to. Another method of imparting an attractive ‘bloom’ to a raw cane sugar is to treat it with stannous chloride. The writer has found

² The sucrose and raffinose were estimated by the method of double polarisation.

quantities of stannous chloride approximating to 0.001 p.c. in raw sugars.

Cane crystals.—These resemble the corresponding beet product, but give a lower polarisation, *e.g.* 99.6 to 99.8 p.c., owing to the presence of a small amount of reducing sugars. They may be distinguished easily from the beet product by their pleasant aroma.

Refined sugars.—As produced in this country, refined sugars are sent out at so high a degree of purity that it has been said that no other chemical substance is sold so pure. The ash content is usually less than one part in ten thousand. To give them a white lustre they are often mixed with a minute trace of ultramarine or other blue colouring matter.

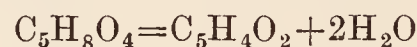
Estimation of galactose and galactans.—It is a special property of galactose and of all compounds containing a galactose residue to give mucic acid when oxidised with nitric acid. When the oxidation is carried out under standard conditions, the galactose or galactose residue may be estimated from the weight of mucic acid obtained. Among the sugars containing a galactose residue may be mentioned lactose, melibiose, raffinose, rhamnose, &c., whilst a number of polysaccharides, *e.g.* galactans and galactopentosans contain this residue. Many of these are constituents of the gums of commerce, whilst the so-called pectins found in apples, pears, grapes and other fruits, as well as in beet-roots, carrots and the tissues of many plants, yield galactose and arabinose on hydrolysis with acids. Just as the formation of furfural constitutes a specific method for the detection and estimation of pentoses and pentosans, so also does the formation of mucic acid form a specific method for the detection and estimation of galactose and galactans. The first chemists to suggest this method of analysis were Tollens and his pupils, and the latest instructions for carrying out the method as revised by the A. O. A. C. (Bull. 107 [revised], U.S. Bur. of Chem., p. 55) are the following:

‘Extract a convenient quantity of the substance, representing from 2.5 to 3 grms. of the dry material, on a hardened filter with five successive portions of 10 c.c. of ether; place the extracted residue in a beaker about 5.5 cms. in diameter and 7 cms. deep, together with 60 c.c. of nitric acid of 1.15 sp.gr., and evaporate the solution to exactly one-third its volume in a water bath at a temperature of 94°–96°C. After standing 24 hours, add 10 c.c. of water to the precipitate, and allow it to stand another 24 hours. The mucic acid has in the meantime crystallised, but it is mixed with considerable material only partially oxidised by the nitric acid. Filter the solution, therefore, through filter paper, wash with 30 c.c. of water to remove as much of the nitric acid as possible, and replace the filter and contents in the beaker. Add 30 c.c. of ammonium carbonate solution, consisting of 1 part ammonium carbonate, 19 parts of water and 1 part strong ammonium hydroxide, and heat the mixture on a water bath at 80°C., for 15 mins., with constant stirring. The ammonium carbonate takes up the mucic acid, forming the soluble mucate of ammonium. Then wash the filter paper and contents several times with hot water by decantation, passing the washings through a filter

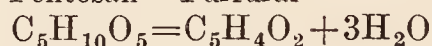
paper, to which finally transfer the material and thoroughly wash. Evaporate the filtrate to dryness over a water bath, avoiding unnecessary heating which causes decomposition, add 5 c.c. of nitric acid of 1.15 sp.gr., thoroughly stir the mixture and allow to stand for 30 mins. The nitric acid decomposes the ammonium mucate, precipitating the mucic acid; collect this on a tared filter or Gooch crucible, wash with from 10 to 15 c.c. of water, then with 60 c.c. of alcohol and a number of times with ether; dry at the temperature of boiling water for 3 hours, and weigh. Multiply mucic acid by 1.33, which gives galactose, and multiply this product by 0.9 which gives galactan.’

As will be seen, the method is empirical, the yield of mucic acid falling short in all cases of the theoretical.

Estimation of pentoses and pentosans.—The pentoses, arabinose and xylose, containing as they do a free carbonyl group, may be estimated by cupric reduction methods. Pentosans, on the other hand, do not reduce alkaline copper solutions. Since, however, pentoses as well as pentosans are usually associated with hexoses, a selective method is necessary for their estimation. It has long been known that many carbohydrates yield furfural when heated with acids, and traces are formed from the ordinary hexoses under these conditions. The pentoses and pentosans, however, when distilled with hydrochloric acid under appropriate conditions can be made to yield 75 to 90 p.c. of the theoretical quantity of furfural indicated by the equations:



Pentosan Furfural



Pentose Furfural

For the elaboration of methods depending on this principle, we are indebted to Tollens and his pupils. Standard conditions of distillation having been established, it was proposed to precipitate the furfural as phenylhydrazone. This, however, necessitated neutralising the distillate, besides involving the difficulty that furfuralphenylhydrazone is a very unstable substance of low melting-point. Furfural is now precipitated as phloroglucide. The latest modification of the method is that of Tollens and Kröber (J. für Landwirtsch. 1909, 335, 1901, 7). The following are its details. A Wurtz flask of 300 c.c. capacity is provided with doubly-bored cork so as to take a dropping funnel and the connecting tube to the condenser. The dropping funnel has a cylindrical reservoir with two graduation marks at 30 c.c., and 60 c.c. respectively. The flask is heated in a bath of Rose’s alloy which melts near 100°C. Its composition is 1 part lead, 1 part tin and 2 parts bismuth. From 2 to 5 grms. of the substance under investigation, according to the quantity of pentose or pentosan it contains, are placed in the Wurtz flask together with 100 c.c. of hydrochloric acid (sp.gr. 1.06). The flask is connected with the condenser and dropping funnel, which latter is charged with hydrochloric acid (sp.gr. 1.06) up to the upper mark at 60°C. The alloy having been previously heated just above its fusing-point, the flask is immersed in it. Distillation is now

conducted at such a rate that 30 c.c. pass over in from 10–11 mins. after which a further 30 c.c. of acid is introduced by means of the dropping funnel. The distillate is received in a 100 c.c. graduated cylinder, the contents of which are transferred to a beaker from time to time. The process is continued in this way until a drop of the distillate no longer gives a pink coloration with aniline acetate paper.¹ As a rule, it is necessary to distil over from 1 to 12 portions of 30 c.c., depending on the quantity of pentose or pentosan present in the material.

Purification of phloroglucinol (Bull. 107 [Revised], U.S. Bur. of Chem. p. 54). Phloroglucinol, as purchased, is liable to contain diresorcinol and should be tested for this as follows: A small quantity is dissolved in a little acetic anhydride, heated almost to boiling and a few drops of concentrated sulphuric acid added. A violet coloration indicates the presence of diresorcinol. A sample of phloroglucinol which gives more than a faint coloration must be purified by the following method: hydrochloric acid (300 c.c. sp.gr. 1.06) is heated in a beaker and the phloroglucinol (11 grms.) added in small quantities at a time, stirring constantly until almost complete solution has been effected. The hot solution is poured into a sufficient volume of hydrochloric acid of the specific gravity above mentioned so that the total volume is 1500 c.c. The liquid is then allowed to remain aside for several days when the diresorcinol will have crystallised out. The solution should be filtered immediately before using. It may become yellow, but this is of no consequence.

Precipitation of the phloroglucide.—To the distillate from the sample under investigation contained in a 500 c.c. beaker is added sufficient of the phloroglucinol solution that the quantity of phloroglucinol is about double that of the furfural expected. The solution becomes at first yellow and then changes to a greenish black when the phloroglucide $C_{11}H_8O_4$ begins to deposit. It is then made up to 400 c.c. with hydrochloric acid (sp.gr. 1.06), and allowed to remain aside over night. The supernatant liquid is then tested with aniline acetate paper to ascertain if all the furfural has been precipitated, and if so, it is filtered through a tared Gooch crucible. The phloroglucide having been collected on the asbestos, it is washed with 150 c.c. of water, taking care that the washings never drain entirely from the crucible until the final quantity of water is placed over the precipitate. The crucible is then dried in a boiling water oven for 4 hours, being placed on a support so that the perforated portion is free to the air. After cooling in a desiccator, the crucible is again weighed. The weight of pentosan or pentose is ascertained from Table XXIV., which is abridged from the original table of Kröber.

When a mixture of pentosans or pentoses is being dealt with, the mean of araban and xylan values and the arabinose and xylose values respectively should be reported. For weights of phloroglucide outside the limits of the table, Kröber gives the following formulæ:

¹ To prepare aniline acetate paper equal volumes of aniline and water are mixed in a test-tube and glacial acetic acid added drop by drop until the milky emulsion becomes a clear solution. Strips of filter paper are then moistened with this solution and allowed to dry.

For a weight of phloroglucide a under 0.03 grm.

$$\begin{aligned}\text{Weight of furfural} &= (a + 0.0052 \times 0.5170) \\ \text{,, pentoses} &= (a + 0.0052 \times 1.0170) \\ \text{,, pentosans} &= (a + 0.0052 \times 0.8948)\end{aligned}$$

For a weight of phloroglucide a over 0.3 grm.

$$\begin{aligned}\text{Weight of furfural} &= (a + 0.0052 \times 0.518) \\ \text{,, pentoses} &= (a + 0.0052 \times 0.10026) \\ \text{,, pentosans} &= (a + 0.0052 \times 0.8824)\end{aligned}$$

The factor 0.0052 is the weight of phloroglucide which remains dissolved in the 400 c.c. of acid solution.

TABLE XXIV.—*Kröber's Table for estimating Pentoses and Pentosans.*

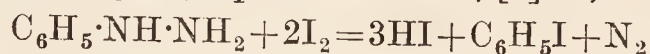
Furfural phloroglucide	Furfural	Ara-binose	Araban	Xylose	Xylan
0.030	0.0182	0.0391	0.0344	0.0324	0.0285
0.040	0.0235	0.0501	0.0441	0.0416	0.0366
0.050	0.0286	0.0611	0.0538	0.0507	0.0446
0.060	0.0338	0.0721	0.0634	0.0598	0.0526
0.070	0.0390	0.0831	0.0731	0.0690	0.0607
0.080	0.0442	0.0941	0.0828	0.0781	0.0687
0.090	0.0494	0.1051	0.0925	0.0872	0.0767
0.100	0.0546	0.1161	0.1022	0.0964	0.0848
0.110	0.0598	0.1270	0.1118	0.1055	0.0928
0.120	0.0650	0.1380	0.1214	0.1146	0.1008
0.130	0.0702	0.1490	0.1311	0.1237	0.1089
0.140	0.0754	0.1600	0.1408	0.1328	0.1169
0.150	0.0805	0.1710	0.1505	0.1419	0.1249
0.160	0.0857	0.1820	0.1602	0.1510	0.1329
0.170	0.0909	0.1930	0.1698	0.1601	0.1409
0.180	0.0961	0.2039	0.1794	0.1692	0.1489
0.190	0.1013	0.2147	0.1889	0.1783	0.1569
0.200	0.1065	0.2255	0.1984	0.1874	0.1649
0.210	0.1116	0.2363	0.2079	0.1965	0.1729
0.220	0.1168	0.2471	0.2174	0.2057	0.1810
0.230	0.1220	0.2579	0.2270	0.2148	0.1890
0.240	0.1271	0.2687	0.2365	0.2239	0.1970
0.250	0.1323	0.2795	0.2460	0.2330	0.2050
0.260	0.1374	0.2903	0.2555	0.2420	0.2130
0.270	0.1426	0.3011	0.2650	0.2511	0.2210
0.280	0.1478	0.3119	0.2745	0.2602	0.2290
0.290	0.1529	0.3227	0.2840	0.2693	0.2370
0.300	0.1581	0.3335	0.2935	0.2784	0.2450

Jolles, in 1905 (Sitzungsber. Wien. Akad. 114, IIb, 1191), worked out a method of estimating furfural which consisted in adding a known quantity in excess of sodium hydrogen sulphite to the faintly acid distillate obtained as already described. The excess (uncombined) sulphite is then estimated by titration with N/10 iodine solution. The method as at present worked out appears to present no advantages over the phloroglucide method.

In 1910, Flohil (Chem. Weekblad. 7, 1057) proposed to estimate furfural by measuring its reducing action on Fehling's solution under standard conditions. His results were revised by Eynon and Lane (Analyst, 37, 41), but even as these chemists left it, the method is inferior in accuracy to the phloroglucide method. J. L. Baker and H. F. E. Hilton (*ibid.* 41, 294) suggest a modification of the copper method which gives more accurate results.

Menaul and Dowell (J. Ind. Eng. Chem. 1919, 11, 1024) have described a gasometric method of estimating pentosans and pentoses, consisting in distilling the substances with dilute sulphuric acid, precipitating with phenylhydrazine acetate in presence of sodium sulphate (instead of sodium chloride) to diminish the solubility of the hydrazone, and adding to the filtrate a 10 p.c.

solution of ammoniacal copper sulphate and collecting and measuring the liberated nitrogen. Ling and Nanji (Bio-Chem. J. 1921, 15, 466) find it more convenient to determine the excess of phenylhydrazine in the filtrate from the hydrazone iodometrically. They find that by distillation with sulphuric acid for 8 hours only 85 p.c. of the possible furfural is obtained. They therefore employ the original method of Tollens and Kröber (*l.c.*), distillation with 12 p.c. hydrochloric acid. A weight of the substance is taken corresponding with about 0.25 gm. of pure pentose, distilled as usual with hydrochloric acid, and the distillate made up to 250 c.c. 25 c.c. is transferred to a 100 c.c. flask, a drop of methyl orange solution added and the hydrochloric acid neutralised with 3N sodium hydroxide, avoiding any rise of temperature. The solution is then slightly acidified with acetic acid, and 10 c.c. of a standard aqueous solution of phenylhydrazine (approximately 2 p.c.) added. The liquid is kept in a water bath at 50°–55°C. for about 20 mins. when the precipitation of the hydrazone is complete. During the precipitation the flask is closed and the surface of the liquid reduced to a minimum by making it up with water to the neck of the flask. This is to avoid atmospheric oxidation. The solution is then cooled, its volume made up to 100 c.c. and filtered through a hardened filter paper. The excess of phenylhydrazine is then determined in an aliquot portion of the filtrate. Into a flask is measured 10 c.c. of *N*/20 iodine solution,¹ and to it is added 10 c.c. of the filtrate from the hydrazone. The liquid is then diluted with water to about 100 c.c. The excess of iodine is titrated with *N*/100 sodium thiosulphate, the volume in c.c.'s being denoted by the symbol *Y*. The titre of the original phenylhydrazine solution employed for the titration is ascertained in an exactly similar manner and the number of c.c.'s of *N*/100 sodium thiosulphate solution is denoted by the symbol *X*. The number of c.c.'s of *N*/100 sodium thiosulphate equivalent to the furfural is *X*–*Y*. The reaction which occurs when phenylhydrazine is added to iodine solution was first ascertained by E. von Meyer (J. pr. Chem. 1887, [2] 36, 115).



The method is quite as accurate as the phloroglucide method, but as it needs more attention it can only be recommended when a large number of determinations have to be made.

The method has recently been thoroughly tested in the writers' laboratories by Mr. A. Churchman.

For the estimation of methyl pentoses or methyl pentosans, see Tollens and Ellet (Ber. 38, 492); Tollens and Mayer (*ibid.* 40, 2441); Jolles (Annalen, 351, 41).

Analysis of mixtures of sugars.—I. *Invert sugar.*—Commercial invert sugar is one of the most valuable and widely-used brewing sugars. It is prepared by hydrolysing raw cane sugars by an acid (usually sulphuric but occasionally hydrochloric)—raw beet sugars cannot be used for this purpose—neutralising with calcium carbonate filtering, and after passing through a

¹ In the original paper the iodine solution employed is stated to be *N*/10, and the thiosulphate *N*/20.

column of animal charcoal concentrating the filtrate to such a degree that a 10 p.c. solution of the final product shows an extract of 70–72 Brewers' lb. per 2 cwt. The extract is determined by weighing out 10 grms. of the sample, dissolving in water, diluting to 100 c.c. and determining the specific gravity of the solution. The excess specific gravity over that of water (taken as 1000), multiplied by the factor 2.24, gives the extract of the sample in lbs. per 2 cwt. This method is quite an arbitrary one, and if a solution of any other concentration than 10 p.c. is made use of, the factor directly proportional to 2.24 does not give the same result.

The estimation of the ash and water is conducted as described on p. 479 (see more especially under syrupy products). The sugars are estimated by a scheme devised by Morris (J. Inst. Brewing, 4, 162). Morris employed the gravimetric method of Brown, Morris and Millar (see p. 468), whilst the writer has always employed the volumetric method (see p. 461). The details of the scheme when the latter method is employed are as follows:—

Total reducing sugars.—A convenient volume (usually 10 c.c.) of a 10 p.c. solution of the sample is made up to 500 c.c. and titrated with 10 c.c. of Fehling's solution in the manner described on p. 461. Let the percentage of apparent invert sugar calculated on the sample be denoted by the symbol *I*.

Sucrose.—The same volume of a 10 p.c. solution as that employed for the estimation of the total reducing sugars is diluted with 100 c.c. of water and 20 c.c. of *N*/2 hydrochloric acid. The mixture is raised to a boiling temperature and maintained in ebullition for one minute, after which it is cooled, neutralised by the addition of 20 c.c. of *N*/2 sodium hydroxide, and made up to 500 c.c. The solution is then titrated against 10 c.c. of Fehling's solution. The percentage of apparent invert sugar calculated on the sample may then be denoted by the symbol *I'*. The percentage of sucrose is then calculated by the following formula: $S = \frac{95(I' - I)}{100}$.

Commercial invert sugar contains unfermentable reducing substances, and it is therefore necessary to correct the results for these. The fermentation test is best carried out as follows: 25 grms. of the sample are dissolved in about 200 c.c. of water in an Erlenmeyer flask and the solution is sterilised by boiling. About 5 c.c. of yeast decoction (1–5) is now added, and about 3 grms. of washed pressed yeast. The flask is closed with a cotton wool plug and placed in a thermostat at 70°F. for 3–4 days, after which it is transferred to a 250 c.c. flask, a little alumina cream added and made up to 250 c.c. The reducing power of the filtrate is then determined and calculated on the sample. To correct the total reducing power for that due to the unfermentable matter, the following formula is made use of: $G = \frac{xy}{x - y}$, in which *x* = the number of c.c.'s of the fermented solution, and *y* the number of c.c.'s of the original unfermented solution required to reduce 10 c.c. of Fehling's solution, both solutions being calculated to the same concentration.

The rotation of a 10 p.c. solution of the sample in divisions Ventzke (2-dm. tube) is determined before and after fermentation. The direct rotation value corrected for that of the fermented solution and for that of the percentage of sucrose found (*see above*) is denoted by the symbol R.

From these data the percentages of dextrose and lævulose in the sample may be calculated by the following simultaneous equations:—

$$(a) (D'D + L'L) \cdot 01 = G$$

$$(b) 0.305D + (-0.531L) = R$$

The values represented by the symbols D' and L' in equation (a) are the gram Fehling equivalents of dextrose and lævulose respectively at a certain concentration; whilst D and L are the symbols for the percentage of dextrose and lævulose respectively; and in equation (b) the readings in a 2-dm. tube in Ventzke divisions for 10 grms. in 100 c.c. The former may be obtained from the table of Ling and Jones (p. 462). If the gravimetric method is used, the constants worked out by Morris (J. Inst. Brewing, 4, 162) for the Brown, Morris and Millar method are applied.

Invert sugar is supplied to the brewer in three grades, and the following are typical analyses of each:

	No. 1	No. 2	No. 3
Dextrose	33.85	36.96	35.44
Lævulose	36.22	35.01	34.85
Sucrose	3.39	1.89	4.54
Albuminoids	0.20	0.26	0.27
Ash	1.57	2.20	2.51
Other organic matter ¹	4.25	5.23	3.60
Water	17.52	18.45	18.79
	100.00	100.00	100.00

These results were obtained with samples of the three grades of invert sugar of high quality. It sometimes happens that there is a shortage of raw cane sugar of low ash content on the market, and some considerable latitude has to be allowed with regard to the permissible limits of ash in the three grades of sugar. The percentages of ash should, however, never exceed the following limits, which will seldom be reached:

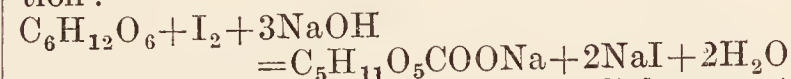
No. I, 2.00 p.c.; No. II, 2.75 p.c.; No. III, 3.50 p.c. The percentage of albuminoids should not exceed the following: No. I, 0.30 p.c.; No. II, 0.50 p.c.; No. III, 0.75 p.c. (compare below).

A widespread belief exists among brewers that invert sugar prepared from beet products gives rise to troubles when employed for brewing, and the writer from practical experience can confirm this in so far as invert sugars prepared from 'raw' beet products are concerned. On the other hand, no exception can be taken to invert sugars prepared from beet crystals and other high-grade sugars derived from beet, except that they do not add to the palate fulness or lusciousness of the finished beers. In seeking an explanation of these facts, it has to be remembered that the substances other than the sugars present in 'raw' products derived from

the sugar cane are helpful in producing that fulness of palate which—especially in the case of mild ales and stouts—is now demanded by the public. It is otherwise in the case of 'raw' beet products. Here the substances, other than the sugars, have a nauseous flavour which tends to impair the palate of beers. These substances appear also to cause certain secondary troubles in the finished beers.

When low-grade beet sugars have been used for the manufacture of invert sugar, the product will possess a characteristic odour and flavour. If, however, higher grade (first runnings) raw beet sugars have been employed, it is difficult to arrive at a decision from the odour and flavour alone, more especially if the sample has been made from a mixture of first running beet sugars and raw cane sugars. The writer would point out in this connection that the percentage of albuminoids (*i.e.* nitrogen $\times 6.25$) in beet products greatly exceeds that in cane products. Thus he has found the following percentages in low-grade cane products: Mauritius, 0.48 p.c.; Penang, 0.39 p.c.; Brazil, 0.63 p.c.; Panela, 0.61 p.c.; Jaggery, 0.59 p.c.; cane molasses, 4–5 p.c. On the other hand, he has found the following percentages in beet products: first runnings, 0.89 to 1.00 p.c.; second runnings, 1.77 to 2.00 p.c.; beet molasses, 6.23 to 9.50 p.c.¹ (Ling, J. Inst. Brewing, 1914, 20, 185).

Direct estimation of aldoses in presence of ketoses.—Romijn has shown (Zeitsch. anal. Chem. 1897, 36, 18, 349) that when standard iodine and caustic soda are added to a solution of aldose and the mixture left for 15–20 mins. and acidified with standard sulphuric acid, some of the iodine is reduced and the excess may be titrated with standard thiosulphate solution using starch as indicator. The reaction in its simplest form may be represented in the case of an aldo-hexose by the following equation:—



Ketoses are only oxidised to a very slight extent by iodine (*cf.* Collin and Lievin, Bull. Soc. chim. 1918, 47, 402; Willstätter and Schüdel, Ber. 1918, 51, 780; Judd, Bio-Chem. J. 1920, 14, 255).

Baker and Hulton (Bio-Chem. J. 1920, 14, 754) have recently investigated this method, and they have modified the procedure as follows: 20 c.c. of N/10 iodine and 30 c.c. of N/10 soda are added to 0.1 gm. of the sugar dissolved in 10 c.c. of water. The mixture is left for 3–5 mins., acidified with N/1 sulphuric acid and the excess of iodine titrated with N/20 thiosulphate using starch as indicator.

For a method of isolating sucrose from the mixture of glucose, fructose, and sucrose, *see* Shigcru Komatsu and Minoru Tanimura (Memoirs of the Coll. of Science, Kyoto Imperial University, Series A., vol. vii.). Invertase and raffinase show the same affinity constants in respect to α - and β -dextrose, to lævulose, and to β -galactose, and these sugars inhibit the action of the two enzymes on sucrose and on raffinose to the same extent. It is concluded that invertase and raffinase are identical. Melibrose shows no affinity for invertase.

¹ The molasses values are quoted from Stammer's analyses.

¹ Containing unfermentable reducing carbohydrates expressed as invert sugar	No. 1	No. 2	No. 3
Brewers' extract per 2 cwt.	3.36	3.62	3.40 p.c.
Tint (Lovibond, 10 p.c. solution 1" cell)	72.8	72.6	72.6 lb.
Specific rotary power $[\alpha]_D$	3.5	8.5	13.0 N.
Ferric oxide (Fe ₂ O ₃)	-11.6°	11.4°	-10.4°.
	0.002	0.003	0.003 p.c.

(Josephson, J. Soc. Chem. Ind. 1924, 43, B. 724).

II. *Honey*.—Since the principal constituent of honey is invert sugar, the scheme just described for the analysis of commercial invert sugar may be used for its analysis. The

following analyses of honey from various sources are due to Campbell Brown (Analyst, 3, 267).

Tibbles (*Foods, their Origin, Composition and Manufacture*, p. 729) gives the following analyses of authentic honeys:—

TABLE XXV.—*The Composition of Honey.—Percentages.*

Source	Water	Lævulose	Dextrose	Sucrose	Wax, pollen, and other insoluble matters	Ash	Other organic matter
England. . .	19·10	36·60	36·55	—	trace	0·15	7·60
Wales . . .	16·40	37·20	39·70	—	trace	0·14	6·56
Normandy . .	15·50	36·88	42·50	—	trace	0·17	4·95
Germany . . .	19·11	33·14	36·58	—	trace	0·17	11·00
Greece . . .	19·80	40·00	32·20	—	1·05	0·15	7·80
Portugal . . .	18·80	37·26	34·94	1·20	1·00	0·14	6·66
Jamaica. . .	19·46	33·19	35·21	2·20	2·10	0·26	7·58
California . .	17·90	37·85	36·01	—	trace	0·11	8·13
Mexico . . .	18·47	35·96	35·47	—	trace	0·07	10·03

Seiber (Biedermann's Centralblatt, 1885, 134), average of sixty analyses.

Dextrose	Lævulose	Sucrose	Water
34·71	39·24	1·08	19·28 p.c.

Hoitsema (Zeitsch. anal. Chem. 38, 429).

	Invert sugar	Sucrose	Wax, pollen, &c.	Ash	Water
Minimum	71·20	0·20	0·02	0·13	8·30 p.c.
Maximum	74·50	2·60	0·46	0·34	17·80 p.c.

Canadian Inland Revenue Bulletin, 47.

	Invert sugar	Sucrose	Ash	Water
Minimum	66·37	0·50	0·03	12·00 p.c.
Maximum	78·80	7·64	0·05	33·00 p.c.

Narbonne Honey (The Practical Grocer, ii. 161).

	Invert sugar	Sucrose	Wax, pollen, &c.	Ash	Water
	74·00	7·10	1·50	0·301	71·0 p.c.

The presence of sucrose in honey seems remarkable. The writer has found as much as 10 p.c. of sucrose in some samples of British honey. Such a high percentage is, however, exceptional.

In the table on p. 477 are given some recent analyses of honey samples made in the writer's laboratories.

Honeys in the United States have been found to contain carbohydrates resembling dextrin, which are precipitable by alcohol from their aqueous solutions and are unfermentable by brewers' yeast. The specific rotatory power of honey dextrin, according to Browne, is $[\alpha]_D^{115^\circ}$ – 160° . Browne (Bull. 110, U.S. Bur. of Chem.) gives a number of analyses of dextrinous honeys of different kinds, and he shows that the quantity of dextrin varies from 0·34 to 12·95 p.c.

Honey is frequently adulterated with artificial invert sugar, and for the detection of the latter certain colorimetric tests have been devised (cf. Behre, (J. Soc. Chem. Ind. 1921, 596 A; 1922, 71 A; F. Auerbach and E. Bodländer, Zeitsch. Nahr. Genussm. 1924, 47, 233; J. Soc. Chem. Ind. 1924, 43, B. 567). Furfural is said to be a constituent of artificial invert sugar and C. A. Browne (Bull. 110, U.S. Bur. of Chem.) suggests testing for this with aniline acetate. The reagent

must be freshly prepared by the following method: 5 c.c. of aniline are shaken with 5 c.c. of water and 2 c.c. of glacial acetic acid added. This amount of acid is just sufficient to produce a bright solution. One to two c.c. of the reagent are allowed to flow down the walls of a test-tube into a solution of the honey in an equal weight of water. If, after shaking, a red ring forms below the aniline layer and gradually spreads to the whole solution, invert sugar is present.

Fiehe (Chem. Zeit. 32, 1045; Zeitsch. Nahr. Genussm. 1908, 75) points out that during the manufacture of invert sugar some of the lævulose is converted into β -hydroxy- δ -methylfurfural, which gives a red coloration with a solution of one part of resorcinol in 100 parts of hydrochloric acid (sp.gr. 1·19). This has been confirmed as a test for artificial invert sugar (see Witte, Zeitsch. Nahr. Genussm. 1909, 625; Reinhardt, *ibid.* 1910, 113; Muttelet, Ann. Falsif. 3, 206).

More recently, Litterscheid (Chem. Zeit. 37, 321) has stated that the following colorimetric method may be used for the detection of artificial invert sugar in honey: 10–20 grms. of the honey are successively triturated with two portions of 10 c.c. of ether in which one or two crystals of β -naphthol have been previously dissolved. The unfiltered extract is transferred to a shallow porcelain dish and left in a dark place until the ether has evaporated. Four or five c.c. of concentrated 88–90 p.c. sulphuric acid are added to the residue, the latter being completely moistened with the acid, and allowed to stand. A dirty yellowish or reddish-yellow colour, which in half an hour becomes dirty yellowish-green, is obtained with natural honey, whilst a Bordeaux red to bluish-violet colour appears in the course of half an hour in the case of honey containing commercial invert sugar. A positive result was obtained with mixtures of natural honey and 5 p.c. of commercial invert sugar, and sometimes also when the result obtained by Fiehe's method (*l.c.*) was inconclusive.

These tests are for the detection of artificial

	No. 1 Purchased as "pure honey." Probably for the most part com- mercial invert sugar	No. 2 Pure 1920 honey. Granulated mostly from clover and bramble. "Fine quality "	No. 3 1919 honey. Con- taining a little honey dew, which accounts for the dark colour. "Quality poor "	No. 4 Pure honey, 1920. Chiefly from heather, " Good quality "
Dextrin . . .	1·37	1·37	1·20	trace
Dextrose . . .	33·02	37·02	34·33	35·73
Lævulose . . .	37·04	37·23	32·62	35·59
Water . . .	15·58	17·16	17·11	19·94
Ash . . .	0·14	0·30	0·45	0·60
Albuminoids . . .	0·40	0·80	0·85	1·90
Cane sugar . . .	Nil	Nil	Nil	Nil
Other organic matter (by difference) *	12·45	6·12	13·44	6·44
	100·00	100·00	100·00	100·00
* Pentosans . .	2·25 p.c.	1·1 p.c.	1·0 p.c.	0·8 p.c.

honey. For the detection of genuine honey, it has been suggested to apply a physiological (serum) test (Langer, Arch. Hygiene, 71, 308), and it has also been proposed to characterise natural honey by determining its catalytic and invertive powers (Auzinger, Zeitsch. Nahr. Genussm. 1911, 65).

Useful bibliographies of honey are published by the U.S. Department of Agriculture. Bull. 13 gives a list of papers from 1867 to 1892. Bull. 110 continues the bibliography to 1908, whilst it was brought to 1910 by Muttelet (Monit. Scient. 74, 152). The lists are published in the Journal of the Society of Chemical Industry (1892, 11, 761 ; 1911, 30, 702).

III. *Brewing glucose or glucose chips*.—This description of sugar occupies a position next in importance to invert sugar as a brewing sugar. It is prepared by the hydrolysis of different kinds of starch with acids. This material consists for the most part of dextrose, but contains also maltose and dextrans or more probably malto-dextrans. The occurrence of maltose as an intermediate product in the hydrolysis of starch by acids was assumed by numerous observers on the sole evidence of the optical and reducing values obtained with them. Ost, however (Zeitsch. angew. Chem. 1904, 1663), succeeded in isolating maltose from the products of the hydrolysis of starch by acids. Chemists are therefore quite justified in interpreting these products from their constants in terms of dextrose, maltose and dextrans.

The analysis of these products is conducted on the same lines as that of invert sugar, but since the assumed proximate constituents are different, the results must be calculated by different equations. In the following equations D is the symbol for the percentage of dextrose and M that for maltose. The same remarks apply in regard to the coefficient D' as in the case of the corresponding equation for invert sugar; also for the coefficient M' which is a constant for the whole range of dilutions employed (see table of Ling and Jones, p. 462).

Inasmuch as these products contain reversion carbohydrates, the residue after fermentation

is always dextro-rotatory, and in some cases a considerable correction has to be applied to the rotatory power to obtain the value denoted by the symbol G. Brewing glucoses, unlike invert sugars, however, do not contain sucrose.

The equations for calculating the percentage of dextrose and maltose in these products are as follows :—

(a) $(D'D + M'M) \cdot 01 = G$
(b) $0\cdot305D + 0\cdot797M = R$

The following is an analysis of a high-grade sample of glucose chips :—

Dextrose . . .	66·76
Maltose . . .	3·96
Albuminoids . . .	0·53
Ash . . .	1·75
Reversion carbohydrates and other organic matter . . .	13·60
Water . . .	13·40
	100·00

Brewers' extract per 2 cwt. . .	76·1 lb.
Tint (Lovibond, 10 p.c. solution 1' cell) . . .	10·0 N.
Specific rotatory power . $[\alpha]_D$	50·8°

This analysis can scarcely be taken as typical, since these products vary enormously in composition. Thus, the percentage of total sugars ranges from 65 to 75 and the extract from 72 to 76 lbs. The percentage of maltose may also vary from 12 p.c. to *nil*. The specific rotatory power ranges from $[\alpha]_D$ 44° to 56°.

IV. *Glucose syrup or dextrin-maltose*.—This product, which is semi-hydrolysed starch, is largely employed in confectionery and also, though to a lesser extent, in brewing. The analysis is conducted on the same lines as that of solid glucose. The percentage of dextrin is calculated from the rotatory power of a 10 p.c. solution after fermentation by dividing by the factor 11·66 (see p. 452). The factor to be employed really diminishes with the reducing power of the dextrin, but for practical purposes this may be ignored. A typical analysis of glucose

syrup, the composition of which is remarkably constant, is the following :—

Dextrose	23·10
Maltose	26·03
Dextrin	32·17
Albuminoids	0·22
Ash	0·48
Water	18·00
	<hr/>
	100·00

Brewers' extract per 2 cwt. . 70·7 lb.
Specific rotatory power $[\alpha]_D$ 113·1°

Estimation of sugars as phenylosazones.—Maquenne (Compt. rend. 112, 799) determined the yield of phenylosazones from dextrose, lævulose and sucrose,¹ and subsequently Lintner and Kröber (Zeit. ges. Brauw. 18, 153) made an attempt to estimate certain sugars as phenylosazones. The method would be chiefly of service in separating dextrose and lævulose which form phenylglucosazone sparingly soluble in hot water from maltose which yields a phenylosazone readily soluble in hot water. In their studies on the hydrolysis of starch by malt diastase, Ling and Davis (J. Inst. Brewing, 8, 475; Chem. Soc. Trans. 85, 16) used the osazone method to demonstrate the production of dextrose at the later stages of the reaction. They also used the osazone method for the approximate estimation of dextrose as phenylglucosazone in presence of the other starch conversion products (*cf.* also Ling, J. Inst. Brewing, 9, 448). The method is useful as a qualitative one for identifying dextrose in presence of maltose, but it can also be made approximately quantitative. For this purpose it is necessary to employ only the purest freshly distilled phenylhydrazine and also to establish the yield of glucosazone in presence of mixtures of the same sugars contained in the substance under investigation. Ling and Rendle (Analyst, 29, 243) were able to prove the presence and approximate percentage of dextrose in commercial malt extracts known to be unadulterated. Baker and Dick (*ibid.* 30, 79), repeating Grimbert's work on the detection and estimation of small quantities of maltose in presence of dextrose, by treating the mixed phenylosazones with dilute (20 p.c.) acetone, found that the method could not be relied upon for quantitative purposes.

Estimation of lactose in milk by the polarimeter.—For this purpose the A. O. A. C. give the following method (Bull. 107, revised, U.S. Bur. of Chem. p. 118). The normal weight for hydrated lactose $C_{12}H_{22}O_{11} \cdot H_2O$ on the Ventzke instrument is 32·9 grms. Since the percentage of lactose in milk only amounts to 2·8 p.c., double this weight of milk is taken. Instead of weighing it is convenient to measure the milk, and the following table gives the volumes of milk at different specific gravity corresponding to 65·8 grms. See also Bacharach, Analyst, vol. xlviii. 1923, p. 521.

It is pointed out that for ordinary purposes a pipette graduated to deliver 64 c.c. is sufficiently exact for all milks.

¹ Sucrose gives a certain amount of phenylglucosazone when heated with phenylhydrazine and acetic acid in virtue of undergoing partial hydrolysis.

TABLE XXVI.—*Volumes of Milk corresponding to the Double Normal Weight of Lactose.*

Specific gravity of milk	Volume of milk for a lactose double normal weight (Ventzke scale)
	c.c.
1·024	64·25
1·025	64·20
1·026	64·15
1·027	64·05
1·028	64·00
1·029	63·95
1·030	63·90
1·031	63·80
1·032	63·75
1·033	63·70
1·034	63·65
1·035	63·55
1·036	63·50

The milk is clarified with a solution of mercuric nitrate, or with one of mercuric iodide. These are prepared as follows :—

Mercuric nitrate.—Metallic mercury is dissolved in twice its weight of nitric acid (sp.gr. 1·42), and the solution diluted with an equal volume of water.

Mercuric iodide.—Potassium iodide (33·2 grms.) is added to a solution of mercuric chloride (13·5 grms.), dissolved in glacial acetic acid (20 c.c.) and water (640 c.c.).

The volume of milk equivalent to the double normal weight of lactose is measured into a flask having a mark at 102·6 c.c. For clarification either 1 c.c. of the mercuric nitrate solution may be used or 30 c.c. of the mercuric iodide solution (an excess of either reagent is without effect). The mixture is made up to a volume of 102·6 c.c., the 2·6 c.c. being the estimated volume of the precipitated casein and fat. After shaking, the liquid is filtered and polarised in a 4-dm. tube. The reading divided by four gives the percentage of lactose in the milk.

Other methods have been devised for the estimation of lactose in milk. Thus, Wiley and Ewell (Analyst, 21, 182), Leffman and Beam (Analysis of Milk and Milk Products, 1896, p. 39). Richmond has also dealt with the estimation of lactose in milk (*see* article on MILK, vol. iv. p. 370).

Lactose exhibits the phenomenon of mutarotation, and when solid products are polarised the solution must be allowed to remain until a constant reading is obtained, or the mutarotation must be destroyed by making up the solution in presence of a little alkali or ammonia. This applies to other sugars which exhibit mutarotation, *e.g.* dextrose, lævulose, &c.

Biochemical methods of estimating sugars.—The only methods of this class which will be alluded to here are those depending on the selective fermentability of different sugars by different yeasts. The fermentation method has already been mentioned in connection with the estimation of carbohydrates of the dextrin class in presence of fermentable sugars (*see* pp. 474–477). The better known monohexoses, *d*-mannose, lævulose, dextrose and galactose, are fermentable by *Saccharomyces cerevisiæ*, *S. pastorianus* and *S. ellipsoideus* (not, however, the monopentoses,

arabinose and xylose), as are also the bioses, sucrose and maltose. These latter, however, must in the first place be hydrolysed to dextrose and lævulose and dextrose respectively. Consequently, for a yeast to be able to ferment sucrose, it must contain invertase or sucrase, whilst to ferment maltose it must contain maltase. Lactose is unfermentable by the above-mentioned yeasts which do not contain lactase, but Fischer and Tierfelder (Ber. 27, 2031) describe a yeast which ferments milk sugar as well as the ordinary monohexoses, but does not ferment maltose.

S. Marxianus does not contain a maltase or a lactase. Consequently, whilst it ferments the ordinary monohexoses, the bihexoses, lactose and maltose are unfermentable by it. Baker and Dick (Analyst, 30, 79) found that maltose could be detected in mixtures of that sugar and the ordinary monohexoses by fermenting the latter with *S. Marxianus*. Davis and Daish (*l.c.*) give the conditions under which maltose may be estimated in the mixture of that sugar with dextrose, lævulose or sucrose, by means of one of the three yeasts, *S. Marxianus*, *S. exiguus* or *S. anomalus*, which do not contain maltase. After fermentation the residual reducing power is estimated, and expressed as a percentage of maltose. When pentoses are present a correction must be made for these from a separate determination.

Several observers have made use of the fact that lactose is unfermentable by ordinary yeasts, *e.g.* *S. cerevisiæ*, to estimate that sugar in admixture with the fermentable sugars. The writer finds this method to give fairly satisfactory results. It has been investigated by Baker and Hulton (Analyst, 35, 512).

In all these laboratory fermentations, it is necessary to add a certain quantity of yeast food, which may consist of Hayduck's solution: potassium phosphate (25 grms.), magnesium sulphate (8 grms.), and asparagine (20 grms.) dissolved in water and made up to one litre. One cubic centimetre of this solution to each 25 c.c. of liquid to be fermented is used. The writer usually employs, however, yeast decoction as a yeast food in these cases (*see p.* 474). The fermentations may be conveniently carried out in Erlenmeyer flasks plugged with cotton wool. The flasks must be of sufficient size so that the liquid never reaches the cotton wool during the fermentation.

Estimation of mineral matter (ash) in sugar products.—The estimation of the ash in sugars, molasses, &c., by direct incineration, is not only a lengthy and tedious operation, but it is very difficult and often impossible to obtain concordant results in repetition experiments. Thus the mineral residues obtained by burning commercial sugars consist largely of alkali carbonates, which are fusible and volatile at the temperature at which the incineration is sometimes conducted. When fusion occurs before all the carbon has been burnt, the latter is occluded in a fused mass of mineral matter and complete combustion is then impossible. The procedure recommended by the A. O. A. C. (Bull. 107 [revised] U.S. Bur. of Chem. 67–68) is as follows: 'Heat from 5 to 10 grms. of sugar molasses, &c., in a platinum dish of 50–100 c.c. capacity at 100°C. until the water has been expelled and then slowly over a flame until

intumescence ceases. Then place the dish in a muffle and heat at low redness until a white ash is left.'

The method most frequently employed is that first proposed by Scheibler in which the sugar is burnt in the presence of sulphuric acid. When this method is employed it is not necessary to use platinum capsules, but these may be replaced by porcelain or silica capsules. Indeed, in one respect, the latter are superior to platinum for the purpose, for since porcelain and silica do not conduct heat as well as does platinum, there is not so much danger of the ash fusing should the temperature of the muffle suddenly rise. And here it may be pointed out that on no account should sugar be incinerated over a flame, but always in a muffle furnace which should be kept at a low red heat.

The plan of carrying out the estimation of sulphated ash, which the writer has adopted for many years, is as follows. A portion of the sample (5 or 3 grms.) is accurately weighed out in a recently ignited capsule, 2 c.c. of concentrated sulphuric acid, free from fixed mineral matter, are dropped over the surface and subsequently a little distilled water is added. The addition of water is to equalise the reaction: it is not necessary with syrups and molasses or with very moist solid sugars. The capsule is then heated over a flame until intumescence is complete, when it is transferred to a muffle and incinerated at a low red heat. The resulting ash should be feathery. When fusion occurs this is generally attended by low results unless carbon is present. Some chemists after determining the weight of the ash, dissolve it in water and test it with litmus paper for acidity, but if the above instructions are followed, there is no danger of the presence of sulphuric acid when combustion is complete. Obviously the sulphated ash weighs more than that obtained by direct incineration, and to correct for this, Scheibler's suggestion to deduct one-tenth from the weight of the sulphated ash is practically universally adopted. It is convenient to work on 3 gm. portions of sugars, for in this case multiplication of the weight of the resulting ash by 30 gives the percentage of ash on the sample with Scheibler's correction. In the case of some products, *e.g.* brewing sugars, the deduction of one-tenth from the weight of sulphated ash is undoubtedly too large a correction, but the method gives comparative rather than absolute accuracy, and the latter, as already observed, cannot be attained by the direct incineration method.

Sand.—When sand is present and it is desired to estimate it, the ash is dissolved in the capsule in a little warm dilute hydrochloric acid, and, after allowing the sand to subside, the supernatant liquor is decanted off. The sand is now washed by decantation, dried, ignited and weighed. In most books, instructions are given to collect the sand on a paper filter, and after washing out the soluble matter to burn the filter. Filtration is, however, quite unnecessary.

Soluble ash.—This is the difference between the total ash and the sand. In case any silica, derived from soluble silicates in the sample, had been included in the latter, a slight error would be introduced. This, however, is quite negligible. On the other hand, low grade raw cane products frequently contain wood

fragments of sugar cane, and other insoluble extraneous matters, and the total ash taken as above includes the ash of these extraneous matters. The true soluble ash must be estimated on a known volume of a standard filtered solution of the sugar. Thus, 25 grms. of the sugar are dissolved in water, made up to 100 c.c., and an aliquot portion of the filtrate corresponding with 5 or 3 grms. evaporated and incinerated with sulphuric acid as already described.

Estimation of ash from the electrical conductivity of commercial sugar solutions.—This method was first placed on a practical basis by Main (Seventh Inter. Cong. Appl. Chem. Section V. p. 66; Inter. Sugar J. 11, 334). The subject was investigated by Reichert (Zeitsch. anal. Chem. 28) more than thirty years ago. Main's observations are briefly as follows. For practical purposes, it may be accepted that sugar in solution is a non-electrolyte, and that the conductivity of impure sugar solutions is to be ascribed to the inorganic and organic salts present. If in a series of samples, solutions of the same concentration are made, the resistances of these solutions are inversely proportional to the amount of salts present. The resistances are measured by Kohlrausch's telephone method. Although the sugar in the solutions may be regarded as non-conducting, variations in the quantity of sugar present affect the conductivity of the salts present. The disturbing influence of differences in the quantity of sugar present can be removed by working with solutions of about the same specific gravity. Taking a series of sugars of about the same grade containing from 2 to 5 p.c. of ash, 5 grms. of each are dissolved in distilled water, made up to 100 c.c. and the resistance of the solutions determined at 20°C. Then it is found that the resistances expressed in ohms multiplied by the percentage of ash as determined gravimetrically in the usual manner give approximately a constant which serves for the determination of ash in other samples of similar sugars when the resistance of their solutions is determined in the same manner in the same cell. Thus $A=K/O$, where A is the percentage of ash in the sample, K the constant above referred to, and O the resistance of the solution expressed in ohms. When working with molasses, the samples are diluted to 33 Beaumé and 2 grms. weighed out, diluted to 100 c.c., and the constant determined as in the case of sugars.

The accuracy of which the method is capable may be judged from the following instances cited by Main. Column 1 in the tables gives the resistance in ohms=O. Column 2 gives the percentage of ash estimated gravimetrically=A. Column 3 gives the product $O \times A=K$. Column 4 gives the ash calculated from the mean value of K as already explained.

Sugars.			
O	A	K ¹	A'
132	5.17	682	5.15
167	4.07	680	4.07
199	3.43	683	3.42
212	3.19	676	3.21
220	3.07	675	3.09
293	2.33	683	2.32

¹ The mean value for K is 680.

Molasses.

O	A	K ²	A'
190	8.76	1664	8.80
191	8.75	1671	8.75
194	8.63	1674	8.62
195	8.62	1681	8.57
196	9.56	1678	8.53
202	8.19	1663	8.34

Lange (Zeits. Ver. Deut. Zuckerind. 1910, 359) finds that reliable results can be obtained by Main's method with products, the ash percentages of which do not differ by more than 0.5 p.c. In order to make the method of greater general applicability, the influence of sugar as a non-conductor on the conductivity of a salt solution was further investigated. Where C is the conductivity of the solution containing p grams in 100 c.c. of the non-conductor, c is the conductivity of the aqueous solution of the salt, and a an empirical coefficient, the relationship may be expressed by Arrhenius' formula

$C=c\left(1-\frac{a}{2p}\right)^2$. The value of the coefficient a for the group of salts occurring in sugar products was found by Lange to be 0.0314. In the case of products containing more than 3 p.c. of ash, the conductivity of a series of solutions of different ash content has been determined, and the conductivity which the solutions would have if no sugar were present is calculated by the above formula. From the values thus obtained, a table has been constructed. When dealing with any product, it is simply necessary to determine the conductivity of its aqueous solution, and calculate from this and the known sugar content the conductivity of solution without sugar. The percentage of ash may then be ascertained by the aid of these data from a table. Lange has also constructed an empirical table for products containing less than 3 p.c. of ash, with which the influence of the sugar on the conductivity may be ignored. He has also calculated a table for correcting for the influence of temperature between 15° and 25°C. He gives a number of examples with various products illustrating the accuracy of the method.

Estimation of water and solid matter in saccharine products.—The usual method of estimating water in solid commercial products is to heat from 3 to 5 grms. weighed out to the nearest half milligram in a drying oven at 100°C. for 3 to 5 hours, taking the loss in weight as due to water. In the case of small-grained, very moist sugars containing much molasses, this method gives low results. Better results are obtained if the drying be conducted at 105°–110°C.³ This, however, applies more especially to beet products; in the case of cane products, which usually contain a large amount of reducing sugars, the use of such a temperature would be attended by error due to the decomposition of the latter. If the products be heated in a current of air or other gas, the moisture may usually be expelled from all solid sugar products at 100°C. A simple and convenient apparatus

² The mean value for K is 1672.

³ This temperature was prescribed by the International Commission on the Unification of Methods of Sugar Analysis (Paris, 1900).

for this purpose has been devised by Siau (J. Soc. Chem. Ind. 30, 61). The official method of A. O. A. C. is to be found in Bull. 107 (revised), U.S. Bur. of Chem. p. 64.

The sugar is conveniently weighed out and dried in a shallow metal dish—a copper dish serves the purpose very well—or the drying may be conducted in a porcelain or quartz dish.

Estimation of water in syrups, molasses, and massecuites.—The following directions are given for this purpose by the A. O. A. C. (Bull. 107, l.c.). The methods are not suitable, however, for those products which contain large percentages of reducing sugars, e.g. cane products.

Drying on pumice stone.—‘Prepare pumice stone in two grades of fineness. One of these should pass through a 1 mm. sieve, whilst the other should be composed of particles too large for a millimetre sieve, but sufficiently small to pass through a sieve having meshes 6 mm. in diameter. Make the determination in flat metallic dishes or in shallow, flat-bottomed weighing bottles. Place a layer of the fine pumice stone, 3 mm. in thickness, over the bottom of the dish, and upon this place a layer of the coarse pumice stone from 6 to 10 mm. in thickness. Dry the dish thus prepared and weigh. Dilute the sample with a weighed portion of water in such a manner that the diluted material shall contain from 20 to 30 p.c. of dry matter. Weigh into the dish, prepared as described above, such a quantity of the diluted sample as will yield, approximately, 1 gm. of dry matter. Use a weighing bottle provided with a cork through which a pipette passes if this weighing cannot be made with extreme rapidity. Place the dish in a water oven and dry to constant weight at the temperature of boiling water, making trial weighings at intervals of 2 hours. In case of materials containing much lævulose or other readily decomposable substances, conduct the drying *in vacuo* at about 70°C.’

Drying on quartz sand.—‘In a flat-bottom dish place 6 to 7 grms. of pure quartz sand and a short stirring rod. Dry thoroughly, cool in a desiccator, and weigh. Then add 3 or 4 grms. of the molasses, mix with the sand, and dry at the temperature of boiling water for from 8 to 10 hours. Stir at intervals of an hour, then cool in a desiccator, and weigh. Stir, heat again in the water oven for an hour, cool, and weigh. Repeat heating and weighing until loss of water in one hour is not greater than 3 mgs.

‘Before using, digest the pure quartz sand with strong hydrochloric acid, wash, dry, ignite and keep in a stoppered bottle.’

For the estimation of water in cane products, honey, &c., which contain a considerable amount of reducing sugars, methods of drying in a vacuum have to be resorted to for the reason above alluded to. The method of Carr and Sanborn (Bull. 47, U.S. Bur. of Chem., p. 134) is one of which the reliability has been proved. The method (l.c.) is as follows: Clean fine-grained pumice is divided into fragments of the size of No. 4 shot. The finer particles (dust) are separated from the coarser by passing through a 40-mesh sieve; the two grades are heated separately. They are digested with hot 2 p.c. sulphuric acid and washed until the washings

are neutral. The washing may be carried out rapidly by decantation. The washed pumice is dried by heating to redness in a Hessian crucible, after which it is placed while hot in a desiccator. A thin layer of the dust is placed over the internal surface of the dish in which the estimation is to be conducted. Above this layer are placed sufficient of the larger particles that the dish is almost filled. The dish thus charged with pumice is ignited and weighed, after cooling in a desiccator. The substance to be dried is diluted (if necessary) to a specific gravity of about 1.08 by the addition of water or of alcohol, if no precipitation is caused by the latter. Two or three grms. are distributed uniformly by means of a pipette weighing bottle over the pumice in the dish, the area of which is about 3 sq. ins., i.e. 1 gm. for each square inch of area. The amount of the sample taken is determined by the loss in weight of the weighing bottle after distributing the sample over the pumice. The dish thus charged is placed in a vacuum oven in which a pressure not exceeding 5 ins. of mercury or a temperature not exceeding 70°C. is maintained. The vacuum oven devised by Carr (Browne's Handbook of Sugar Analysis, p. 20) is a convenient apparatus for this purpose.

For removal of the water from pure products, e.g. hydrated dextrose, raffinose, maltose, lactose, &c., the method devised by Lobry de Bruyn and Van Lænt (Rec. trav. chim. 38, 218) may be used. This method was employed by Brown, Morris and Millar (Chem. Soc. Trans. 71, 76) in their work on the products of starch hydrolysis by diastase. Briefly it is carried out as follows: Two small flasks are united by a tube furnished with a stop-cock and a side-tube leading to an air-pump. The substance to be dehydrated is introduced into one of the flasks, the other being partially filled with phosphorus pentoxide. After exhausting the apparatus, the flask containing the substance is immersed in a water, salt water, or oil bath according to the final temperature required, and is slowly heated up to a point at which it ceases to lose weight.

Since in the estimation of water in the liquid or semi-liquid products above referred to, comparative rather than absolute accuracy is required, and expedition being essential, indirect methods of estimating the solid matter (the amount of which is complementary to the water content) are usually resorted to. Two principles are made use of in these indirect methods, one depending on the specific gravities and the other on the refractive indices of sugar solutions. The specific gravities and refractive indices of sugar solutions are both functions of the solid matter present. In most tables, however, the assumption is made that the effect of all sugars is identical on specific gravity and refractive index, which, as will be seen, is not strictly accurate. The two principles will now be discussed *seriatim*.

Specific gravity method of estimating water and solid matter.—A vast amount of labour has been devoted to the determination of the specific gravity of sucrose solutions. In 1854, Balling (Zeits. Ver. Rubenzuckerind. 4, 304) published his well-known tables giving the specific gravities of sucrose solutions of different

concentrations.¹ His tables, which have since been extended by Brix, are now almost universally used on the Continent for determining the density of sugar solutions by means of a spindle. Another table was published by Gerlach in 1863, and this was subsequently recalculated to another temperature by Scheibler. The condensed table (XXVII.) taken from Browne's Handbook, p. 29, shows the relation between the results obtained by different authorities.

TABLE XXVII.—Specific Gravity of Sucrose Solutions by Different Authorities.

Sucrose, p.c. by weight	Balling- Brix, d _{17.5°} C.	Gerlach, d _{17.5°} C.	Gerlach- Scheibler d _{15°} C.	German Imperial Commission	
				d _{15°} C.	d _{20°} C.
0	1.00000	1.00000	1.00000	1.00000	0.99823
5	1.01970	1.01969	1.01978	1.01973	1.01785
10	1.04014	1.04010	1.04027	1.04016	1.03814
15	1.06133	1.06128	1.06152	1.06134	1.05917
20	1.08329	1.08323	1.08354	1.08328	1.08096
25	1.10607	1.10600	1.10635	1.10604	1.10356
30	1.12967	1.12959	1.12999	1.12962	1.12698
35	1.15411	1.15403	1.15448	1.15407	1.15128
40	1.17943	1.17936	1.17985	1.17940	1.17645
45	1.20565	1.20559	1.20611	1.20565	1.20254
50	1.23278	1.23275	1.23330	1.23281	1.22957
55	1.26086	1.26086	1.26144	1.26091	1.25754
60	1.28989	1.28995	1.29056	1.28997	1.28646
65	1.31989	1.32005	1.32067	1.31997	1.31633
70	1.35088	1.35117	1.35182	1.35094	1.34717
75	1.38287	1.38334	1.38401	1.38286	1.37897

Another table which forms the basis of a hydrometer scale very widely used in the sugar and other industries is that of Baumé. This table is based on the specific gravity of solutions of common salt. Table XXVIII., abridged from that given in Browne's Handbook, shows the relation between the various scales. It will be observed that two Baumé scales are given, the new and the old. The latter, although known to be inaccurate, is still retained in many countries.

Table XXIX. is for correcting readings of the Brix hydrometer, taken at different temperatures, to 17.5°C.

In his studies on the products of the hydrolysis of starch, O'Sullivan made use of a divisor for calculating the concentration (grms. per 100 c.c.) from the specific gravity of the solutions. This divisor was the excess specific gravity of a solution of maltose containing 10 grms. in 100 c.c. Brown and Heron subsequently suggested the divisor 3.86, which is the excess specific gravity (calling water 1000) of a solution containing 10 grms. of sucrose in 100 c.c. Comparative accuracy can be obtained with the use of this divisor with solutions containing up to 10 grms. per 100 c.c. of dissolved substance if the specific gravity is corrected for the influence of mineral matter (see below). If the specific gravities of the solutions are expressed in comparison with water as 1000, then obviously the values also express the weights in grams of 1 litre of the solution, or where the specific gravities are taken at 15.5°/15.5° or at any other

¹ It should be pointed out that the solutions used by Balling were standardised on their true percentage of sucrose by weight and not grams per 100 c.c.

TABLE XXVIII.—Specific Gravity of Sucrose Solutions at 17.5°/17.5°C. with Corresponding Degrees Brix and Baumé.

P.c. sucrose by weight or degrees Brix	Specific gravity	Degrees Baumé		P.c. sucrose by weight or degrees Brix	Specific gravity	Degrees Baumé	
		New	Old			New	Old
1.0	1.00388	0.6	0.55	39.0	1.17430	21.8	21.4
2.0	1.01779	1.1	1.1	40.0	1.17943	22.3	21.9
3.0	1.03173	1.7	1.7	41.0	1.18460	22.9	22.4
4.0	1.04570	2.3	2.2	42.0	1.18981	23.4	23.0
5.0	1.05970	2.8	2.8	43.0	1.19505	23.95	23.5
6.0	1.07373	3.4	3.3	44.0	1.20033	24.5	24.0
7.0	1.08779	4.0	3.9	45.0	1.20565	25.0	24.6
8.0	1.10187	4.5	4.4	46.0	1.21100	25.6	25.1
9.0	1.11599	5.1	5.0	47.0	1.21639	26.1	25.6
10.0	1.13014	5.7	5.55	48.0	1.22182	26.6	26.1
11.0	1.14431	6.2	6.1	49.0	1.22728	27.2	26.7
12.0	1.15852	6.8	6.7	50.0	1.23278	27.7	27.2
13.0	1.17276	7.4	7.2	51.0	1.23832	28.2	27.7
14.0	1.18703	7.9	7.8	52.0	1.24390	28.8	28.2
15.0	1.20133	8.5	8.3	53.0	1.24951	29.3	28.75
16.0	1.21566	9.0	8.9	54.0	1.25517	29.8	29.3
17.0	1.23002	9.6	9.4	55.0	1.26086	30.4	29.8
18.0	1.24441	10.1	10.0	56.0	1.26658	30.9	30.3
19.0	1.25884	10.7	10.5	57.0	1.27235	31.4	30.8
20.0	1.27329	11.3	11.1	58.0	1.27816	31.9	31.3
21.0	1.28778	11.8	11.6	59.0	1.28400	32.5	31.85
22.0	1.29231	12.4	12.2	60.0	1.28989	33.0	32.4
23.0	1.29686	13.0	12.7	61.0	1.29581	33.5	32.9
24.0	1.30145	13.5	13.3	62.0	1.30177	34.0	33.4
25.0	1.30607	14.1	13.8	63.0	1.30777	34.5	33.9
26.0	1.31072	14.6	14.35	64.0	1.31381	35.1	34.4
27.0	1.31541	15.2	14.9	65.0	1.31989	35.6	34.9
28.0	1.32013	15.7	15.4	66.0	1.32601	36.1	35.4
29.0	1.32488	16.3	16.0	67.0	1.33217	36.6	35.9
30.0	1.32967	16.8	16.5	68.0	1.33836	37.1	36.4
31.0	1.33449	17.4	17.1	69.0	1.34460	37.6	36.9
32.0	1.33934	17.95	17.6	70.0	1.35088	38.1	37.4
33.0	1.34423	18.5	18.15	71.0	1.35720	38.6	37.9
34.0	1.34915	19.05	18.7	72.0	1.36355	39.1	38.4
35.0	1.35411	19.6	19.2	73.0	1.36995	39.6	38.9
36.0	1.35911	20.1	19.8	74.0	1.37639	40.1	39.4
37.0	1.36413	20.7	20.3	75.0	1.38287	40.6	39.9
38.0	1.36920	21.2	20.8				

temperature, the weight in grams of 1000 fluid grms. of the solution. It follows from this that the concentration (grams per 100 c.c.—100 fluid grms.) can be calculated by the aid of the

formula $C = \frac{S-1000}{d}$, where C is the required

concentration, S is the specific gravity of the solution, and d the excess specific gravity of a 1 p.c. solution of any given pure sugar.

Brown, Morris and Millar (Chem. Soc. Trans. 71, 72) have determined the divisors for sucrose, dextrose, fructose, invert sugar, maltose and certain mixed products of the hydrolysis of starch at various concentrations. Ling, Eynon and Lane (Seventh Inter. Cong. Appl. Chem., Section I. p. 137) have repeated this work for solutions of dextrose, lævulose and maltose. The following may be regarded as the accurate divisors for solutions for the undermentioned sugars containing 10 grms. in 100 c.c. Sucrose, 3.86 (Brown and Heron), dextrose, 3.82 (Ling, Eynon and Lane), lævulose, 3.92 (Ling, Eynon and Lane), invert sugar, 3.87 (mean of dextrose and lævulose values), maltose, 3.91 (Ling, Eynon and Lane). Mixed starch transformation products 3.93–4.01 (Brown, Morris and

TABLE XXIX.

Tempera- ture, degrees Centi- grade	Degrees Brix of solution												
	0	5	10	15	20	25	30	35	40	50	60	70	75
	Corrections to be subtracted from degrees Brix												
0°	0.17	0.30	0.41	0.52	0.62	0.72	0.82	0.92	0.98	1.11	1.22	1.25	1.29
5	0.23	0.30	0.37	0.44	0.52	0.59	0.65	0.72	0.75	0.80	0.88	0.91	0.94
10	0.20	0.26	0.29	0.33	0.36	0.39	0.42	0.45	0.48	0.50	0.54	0.58	0.61
11	0.18	0.23	0.26	0.28	0.31	0.34	0.36	0.39	0.41	0.43	0.47	0.50	0.53
12	0.16	0.20	0.22	0.24	0.26	0.29	0.31	0.33	0.34	0.36	0.40	0.42	0.46
13	0.14	0.18	0.19	0.21	0.22	0.24	0.26	0.27	0.28	0.29	0.33	0.35	0.39
14	0.12	0.15	0.16	0.17	0.18	0.19	0.21	0.22	0.22	0.23	0.26	0.28	0.32
15	0.09	0.11	0.12	0.14	0.14	0.15	0.16	0.17	0.16	0.17	0.19	0.21	0.25
16	0.06	0.07	0.08	0.09	0.10	0.10	0.11	0.12	0.12	0.12	0.14	0.16	0.18
17	0.02	0.02	0.03	0.03	0.03	0.04	0.04	0.04	0.04	0.04	0.05	0.05	0.06
Corrections to be added to degrees Brix													
18	0.02	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.02
19	0.06	0.08	0.08	0.09	0.09	0.10	0.10	0.10	0.10	0.10	0.10	0.08	0.06
20	0.11	0.14	0.15	0.17	0.17	0.18	0.18	0.18	0.19	0.19	0.18	0.15	0.11
21	0.16	0.20	0.22	0.24	0.24	0.25	0.25	0.25	0.26	0.26	0.25	0.22	0.18
22	0.21	0.26	0.29	0.31	0.31	0.32	0.32	0.32	0.33	0.34	0.32	0.29	0.25
23	0.27	0.32	0.35	0.37	0.38	0.39	0.39	0.39	0.40	0.42	0.39	0.36	0.33
24	0.32	0.38	0.41	0.43	0.44	0.46	0.46	0.47	0.47	0.50	0.46	0.43	0.40
25	0.37	0.44	0.47	0.49	0.51	0.53	0.54	0.55	0.55	0.58	0.54	0.51	0.48
26	0.43	0.50	0.54	0.56	0.58	0.60	0.61	0.62	0.62	0.66	0.62	0.58	0.55
27	0.49	0.57	0.61	0.63	0.65	0.68	0.68	0.69	0.70	0.74	0.70	0.65	0.62
28	0.56	0.64	0.68	0.70	0.72	0.76	0.76	0.78	0.78	0.82	0.78	0.72	0.70
29	0.63	0.71	0.75	0.78	0.79	0.84	0.84	0.86	0.86	0.90	0.86	0.80	0.78
30	0.70	0.78	0.82	0.87	0.87	0.92	0.92	0.94	0.94	0.98	0.94	0.88	0.86
35	1.10	1.17	1.22	1.24	1.30	1.32	1.33	1.35	1.36	1.39	1.34	1.27	1.25
40	1.50	1.61	1.67	1.71	1.73	1.79	1.79	1.80	1.82	1.83	1.78	1.69	1.65
50	—	2.65	2.71	2.74	2.78	2.80	2.80	2.80	2.80	2.79	2.70	2.56	2.51
60	—	3.87	3.88	3.88	3.88	3.88	3.88	3.88	3.88	3.82	3.70	3.43	3.41
70	—	5.17	5.18	5.20	5.14	5.13	5.10	5.08	5.06	4.90	4.72	4.47	4.35
80	—	—	6.62	6.59	6.54	6.46	6.38	6.30	6.26	6.06	5.82	5.50	5.33
90	—	—	8.26	8.16	8.06	7.97	7.83	7.71	7.58	7.30	6.96	6.58	6.37
100	—	—	10.01	9.87	9.72	9.56	9.39	9.21	9.03	8.64	8.22	7.76	7.42

Millar). The divisor in all cases increases with a decrease of concentration. In the analysis of commercial products, however, solutions containing 10 grms. per 100 c.c. are usually employed. It has already been mentioned that in applying this method of estimating the concentration of a sugar solution, it is necessary to correct for the influence of the mineral matter. Solutions of most salts have much higher specific gravities for a given concentration than those of the sugars. Heron found that the mean specific gravity of a solution of the sulphated mineral matter containing 1 grm. per 100 c.c. is 1008, and this value in the writer's experience is not far from the truth. The usual plan is to deduct the percentage of ash from the percentage of apparent solids deduced from the specific gravity of a 10 p.c. solution of the sugar by the appropriate factor. The value so obtained subtracted from 100 gives an approximately accurate result. Proteins have very little influence on this method, as the specific gravities of their solutions are so low. To calculate the carbohydrate concentration of beer worts, the writer, after diluting to a specific gravity of about 1040, determines the specific

gravity at 15.5°/15.5°, corrects for ash as above and divides the corrected excess specific gravity by 4. This practice is also adopted by several other chemists.

Refractometric methods of estimating water and solid matter.—The principle and construction of different forms of the refractometer is dealt with in a special article (vol. v. p. 647). These instruments have been applied to a large number of products for several years, but the first to suggest their application to commercial sugars and molasses was apparently Stromer in 1883 (Oest. Ung. Zeit. Zuckerind. 12, 925; 13, 185), who pointed out that the refractive indices and specific gravities of sugar solutions ran parallel to one another. In 1901, Stolle (Zeits. Ver. Deuts. Zuckerind. 51, 469) showed that solutions of sucrose, dextrose, lævulose, and lactose of the same concentration had substantially the same refractive indices. He used the Pulfrich instrument. The next work of importance in this connection is that of Tolmann and Smith (J. Amer. Chem. Soc. 28, 1476), who used an Abbe refractometer. The first to place the refractometric method on a sound practical basis, as regards its application to sugar analysis,

was, however, Main (Inter. Sugar Journ. 9, 481) Main worked with the Abbe refractometer and constructed a table which has since been checked by Schönrock in the laboratories of the Physikalisch-Technische Reichanstalt, Berlin. Schönrock's ¹ results, which are given in Table XXX., show no greater deviation from

TABLE XXX.—*Refractive Index and Water Content of Sugar Solutions.*

$n_D^{20^\circ}$	w	$n_D^{20^\circ}$	w
1.3330	100	1.3883	66
1.3344	99	1.3902	65
1.3359	98	1.3920	64
1.3374	97	1.3939	63
1.3388	96	1.3958	62
1.3403	95	1.3978	61
1.3418	94	1.3997	60
1.3433	93	1.4016	59
1.3448	92	1.4036	58
1.3464	91	1.4056	57
1.3479	90	1.4076	56
1.3494	89	1.4096	55
1.3510	88	1.4117	54
1.3526	87	1.4137	53
1.3541	86	1.4158	52
1.3557	85	1.4179	51
1.3573	84	1.4200	50
1.3590	83	1.4221	49
1.3606	82	1.4242	48
1.3622	81	1.4264	47
1.3639	80	1.4285	46
1.3655	79	1.4307	45
1.3672	78	1.4329	44
1.3689	77	1.4351	43
1.3706	76	1.4373	42
1.3723	75	1.4396	41
1.3740	74	1.4418	40
1.3758	73	1.4441	39
1.3775	72	1.4464	38
1.3793	71	1.4486	37
1.3811	70	1.4509	36
1.3829	69	1.4532	35
1.3847	68	1.4555	34
1.3865	67		

those of Main than 4 in the fourth place of decimals.

Stanek (Zeits. Ver. Deutsch. Zuckerind. 61, 421) determined the corrections to be applied to Main's table, when the observations are made at temperatures other than 20°C. His results are embodied in Table XXXI.

The immersion refractometer (*l.c.*, vol. v. p. 650) has also been employed for sugar products. The range is, however, much less than that of the Abbe instrument, the scale being restricted to solutions containing 21.7 p.c. of sugar and less. The instrument is, however, capable of yielding more accurate results than the Abbe refractometer, since it gives a much sharper border line than the latter.

¹ Schönrock has modified the Abbe refractometer. Instead of glass of refractive index of 1.7 he uses the less refractive flint glass. This enables darker products and more concentrated solutions—up to 85 per cent. concentration—to be examined. The modified instrument is constructed by Messrs. Zeiss & Co.

Comparison of densimetric and refractometric methods.—When either of these methods is applied to commercial products, the assumption is made that the results are affected similarly by all the solid matters present, which is by no means the case. It has been shown above, for example, that the divisors to be applied to the specific gravities of solutions of sugars in order to calculate their concentration, differ according to the particular sugar dealt with, and that they also vary with the concentration of the solution of one and the same sugar. Further, weight for weight mineral matter produces, roughly speaking, twice the effect on specific gravity as do sugars themselves, whilst protein substances have a much lower specific gravity coefficient than have the sugars. Refractometric methods, on the other hand, can be applied over a much wider range of mixtures without impairing their accuracy for practical requirements, than can densimetric methods. Thus, Stanek, working with Main's table, has shown (Zeits. Zuckerind. Böhmen, 34, 5) that with solutions of betaine, sodium formate, potassium formate, sodium acetate, potassium acetate, sodium butyrate, sodium lactate and potassium lactate, a very fair approximation to the truth is obtained with refractometric methods, whilst with densimetric methods the divergences from the truth are considerable. It should be pointed out, however, that whereas refractometric values can only be determined to four significant places, it is easy to measure specific gravities to five significant places.

The writer desires to thank his former assistant, Mr. George McLaren, for making some of the drawings and for help in collecting together the analyses of commercial products recorded in this article.
A. R. L.
D. R. N.

ESTIMATION OF SUGAR IN BLOOD.

Sugar is present as glucose in normal human blood to the extent of about 0.08 p.c.; when it rises above 0.2 p.c. the condition leads to glycosuria. Glucose is also present in the lymph and cerebrospinal fluid.

This sugar is derived from the carbohydrates and proteins of the food, and is utilised by the tissues as a source of energy. The estimation of sugar in the blood is of clinical importance in various pathological conditions, particularly in *diabetes mellitus*. See section on INSULIN at the end of this article. The methods of estimation are complicated by the fact that blood contains many substances which may interfere with the sugar reactions, and in particular, substances such as creatinine and uric acid, which are reducing agents.

A large number of methods have been devised, of which four of the two most satisfactory are described below:—

The blood should be freshly drawn into a vessel containing a few grains of potassium oxalate to prevent coagulation.

It may be obtained from a vein by means of a hollow needle, in which case it is essential that the needle be sharp, or, if a small quantity only is required, from a scratch on the lobe of the ear, or a prick of the finger-tip. Strict

TABLE XXXI.—*Stanek's Correction Table.*

For Determining Water in Sugar Solutions by means of the Abbe Refractometer when Readings are made at other Temperatures than 20°C.

Water per cent.	95	90	85	80	70	60	50	40	30	25	Water per cent.
Tempera- ture C.	To be added to the per cent. of water.										Tempera- ture C.
15°	0·25	0·27	0·31	0·31	0·34	0·35	0·36	0·37	0·36	0·36	15°
16	0·21	0·23	0·26	0·27	0·29	0·31	0·31	0·32	0·31	0·29	16
17	0·16	0·18	0·20	0·20	0·22	0·23	0·23	0·23	0·20	0·17	17
18	0·11	0·12	0·14	0·14	0·15	0·16	0·16	0·15	0·12	0·09	18
19	0·06	0·07	0·08	0·08	0·08	0·09	0·09	0·08	0·07	0·05	19
To be subtracted from the per cent. of water.											
21	0·06	0·07	0·07	0·07	0·07	0·07	0·07	0·07	0·07	0·07	21
22	0·12	0·14	0·14	0·14	0·14	0·14	0·15	0·14	0·14	0·14	22
23	0·18	0·20	0·20	0·21	0·21	0·21	0·23	0·21	0·22	0·22	23
24	0·24	0·26	0·26	0·27	0·28	0·28	0·30	0·28	0·29	0·29	24
25	0·30	0·32	0·32	0·34	0·36	0·36	0·38	0·36	0·36	0·37	25
26	0·36	0·39	0·39	0·41	0·43	0·43	0·46	0·44	0·43	0·44	26
27	0·43	0·46	0·46	0·48	0·50	0·51	0·55	0·62	0·50	0·51	27
28	0·50	0·53	0·53	0·55	0·58	0·59	0·63	0·70	0·57	0·59	28
29	0·57	0·60	0·61	0·62	0·66	0·67	0·71	0·78	0·65	0·67	29
30	0·64	0·67	0·70	0·71	0·74	0·75	0·80	0·86	0·73	0·75	30
Water per cent.	95	90	85	80	70	60	50	40	30	25	Water per cent.

asepsis must be observed, the skin should be cleaned by rubbing with cotton wool dipped in ether, and the instrument must be sterilised. The blood should be drawn without in any way causing fright, pain, excitement, or struggling, as these conditions cause variations in the sugar content. It may be allowed to flow into a dry test-tube containing a little potassium oxalate, from which it can be measured, or it may be aspirated directly into an Ostwald pipette, in the tip of which are a few grains of potassium oxalate.



FIG. 30.

In the quantitative determination of the sugar two distinct processes are involved.

(1) The removal of the blood proteins.

(2) The determination of the sugar in the protein free filtrate.

The method of Folin and Wu (J. Biol. Chem. 1919, 38, 81 ; 1920, 41, 367).—A measured volume of blood is diluted with 7 volumes of water, and mixed with 1 volume of 10 p.c. sodium tungstate (Na₂WO₄.2H₂O). 1 volume of $\frac{2}{3}$ N sulphuric acid is added and the mixture shaken. By this means the proteins are precipitated, and the sugar can be estimated in the filtered liquid.

Solutions required :—

(1) A standard sugar solution, made by dissolving 1 gram. of pure anhydrous glucose in water and diluting to 100 c.c. A few drops of xylenc or toluene are added.

(2) Alkaline copper solution: 40 grms. of anhydrous sodium carbonate are dissolved in about 400 c.c. of water, and are transferred to a

litre flask, 7·5 grms. of tartaric acid are added, and when this has dissolved, 4·5 grms. of crystallised copper sulphate are added, and the liquid is made up to 1 litre.

(3) Molybdate-phosphate solution: 35 grms. of molybdic acid and 5 grms. of sodium tungstate are mixed with 200 c.c. of 10 p.c. sodium hydroxide and 200 c.c. of water. The liquid is boiled vigorously for 20–40 minutes, cooled, diluted to 350 c.c., and to it are added 125 c.c. of concentrated 85 p.c. phosphoric acid. The solution is then diluted to 500 c.c. It gives an intense blue colour with cuprous oxide.

Method.—2 c.c. of the blood filtrate are transferred to a special tube, as shown in the annexed figure, and into two other similar test tubes, graduated at 25 c.c., are put 2 c.c. of standard sugar solution, containing respectively 0·2 and 0·4 mgrms. of glucose. To each tube are added 2 c.c. of the alkaline copper solution. The surface of the mixture must now have reached the constricted part of the tube. The tubes are transferred to a boiling water-bath and are heated for 6 minutes. They are then put into a cold water-bath and cooled without shaking for 2–3 minutes. To each are added 2 c.c. of the molybdate phosphate solution, which dissolves the cuprous oxide that has been formed. The resulting blue solution is diluted to 25 c.c. and well shaken to mix thoroughly, each tube being closed by a rubber stopper. The liquids are then compared in a colorimeter. The depth of the standard in mm. \times 100, and divided by the reading of the unknown, gives the sugar content in mgrms. per 100 c.c. of blood.

Ponder and Howie (Bio-Chem. J. 1921, 15,

170), by the use of pipettes accurately calibrated by weight to deliver 0.4 c.c. and 0.2 c.c., have applied the method of Folin and Wu to the estimation of sugar in quantities less than 1 c.c. of blood.

(2) *The method of Maclean* (Bio-Chem. J. 1919, 13, 135).—The protein is removed from the blood by heating with acid sodium sulphate, and the subsequent addition of dialysed iron. The liquid is filtered, and the sugar in an aliquot part of the filtrate is estimated by boiling under standard conditions with an alkaline solution of copper sulphate containing potassium iodide and potassium iodate.

After boiling, the liquid containing the cuprous oxide in suspension is cooled. No oxidation takes place during this process, as the cuprous oxide is not in solution. The liquid is then treated with slight excess of hydrochloric acid. This interacts with the potassium iodide and iodate liberating iodine equivalent to the amount of potassium iodate in the solution. At the same time the cuprous oxide is dissolved, and is oxidised immediately by some of the free iodine to the cupric condition. The amount of the unused iodine is ascertained by titration

with $\frac{N}{100}$ sodium thiosulphate. The number of c.c. required is denoted by B.

The total quantity of iodine available is determined by taking the same volume of copper and iodate solution as was used for the sugar titration, acidifying, and titrating with the thiosulphate. The number of c.c. required is denoted by A.

Then $A-B$ =the iodine absorbed, which is proportional to the cuprous oxide formed, which is proportional to the sugar present.

Solutions required for the estimation of the sugar in 1 c.c. of blood :

- (1) Sodium sulphate (pure) . 150 grms.
Glacial acetic acid . . 3 c.c.
Distilled water to . . 1000 c.c.
- (2) Dialysed iron (sp.gr. 1.047).
- (3) Potassium bicarbonate . 20 grms.
Potassium carbonate(anhyd.) 15 "
Copper sulphate (cryst.) . 0.7 "
Potassium iodate . . 0.11 "
Potassium iodide . . 1.0 "
Distilled water to . . 100 "

In solution (3) the potassium bicarbonate is dissolved in 60–70 c.c. of distilled water, by gently heating (not above 37°C.) the potassium carbonate is added, and then the copper sulphate which has been separately dissolved, lastly the iodide and iodate are introduced and the solution made up to 100 c.c.

This solution is standardised as regards its iodine content, by taking 3 c.c. and adding to it 10 c.c. of solution (1). To this mixture 10 c.c. of 20 p.c. hydrochloric acid are added. After effervescence has ceased, the liquid is titrated with $\frac{N}{100}$ sodium thiosulphate solution, using starch as an indicator. Number of c.c. required=A.

- (4) $\frac{N}{100}$ thiosulphate solution.

$\frac{N}{10}$ sodium thiosulphate is standardised against $\frac{N}{10}$ potassium dichromate as follows:

20 c.c. of $\frac{N}{10}$ potassium dichromate are mixed with 10 c.c. of 10 p.c. potassium iodide and 5 c.c. of strong hydrochloric acid, on shaking 0.254 gm. of iodine are liberated, this is titrated with the thiosulphate.

$\frac{N}{100}$ thiosulphate is prepared by dilution of the $\frac{N}{10}$ solution.

Procedure when 1 c.c. of blood is used.—26 c.c. of solution (1) are run into a small flask fitted with a rubber stopper, through which passes a glass tube terminating in a capillary point. 1 c.c. of blood is measured into the flask, the stopper is inserted, and the contents raised to incipient boiling. The flask is then allowed to stand for 1–2 minutes, and 3 c.c. of dialysed iron are added. The flask is cooled, and the contents filtered through starch-free filter-paper. Of the filtrate 20 c.c. are taken (or 10 c.c. if glycosuria be present, in which case the total volume is made up to 20 c.c. by the addition of 10 c.c. of solution (1)), and measured into a small conical flask. 3 c.c. of solution (2) are added, and the mixture heated. The liquid should be brought to the boiling-point in 1 minute 40 seconds, and the boiling should be maintained for 6 minutes.

The flask is then cooled, and 10 c.c. of 20 p.c. hydrochloric acid are added. After effervescence stops the liquid is titrated with $\frac{N}{100}$ thiosulphate. The number of c.c. required=B. The amount of glucose present is calculated from the table.

TABLE FOR 1 C.C. OF BLOOD.

Glucose m.g.	A-B	Glucose m.g.	A-B
0.2	→ 0.55	1.2	→ 4.36
0.3	0.95	1.3	4.71
0.4	1.34	1.4	5.07
0.5	1.76	1.5	5.42
0.6	2.16	1.6	5.78
0.7	2.52	1.7	6.13
0.8	2.88	1.8	6.49
0.9	3.27	1.9	6.84
1.0	3.65	2.0	7.20
1.1	4.00		

Method for 0.2 c.c. of Blood.

Solution (1) :

Sodium sulphate . . . 150 grms.
Glacial acetic acid (this should not be added until the solution is ready for use) . . . 1 c.c.
Distilled water to . . . 1000 "

Solution (2) :

Potassium bicarbonate . . 12 grms.
Potassium carbonate (anhyd.) . 8 "
Copper sulphate (cryst.) . . 0.35 "
Potassium iodate . . . 0.05 "
Potassium iodide . . . 0.5 "
Distilled water to . . . 100 c.c.

Solution (2) is standardised by taking 2 c.c. to 10 c.c. of solution (1) and adding 2 c.c. of 75 p.c. hydrochloric acid. It is titrated with $\frac{N}{400}$ thiosulphate.

In estimating the blood 23·8 c.c. of solution (1) are measured into a conical flask, 0·2 c.c. of blood are added. The further procedure is as in the previous method, only 1 c.c. of dialysed iron is added. To 20 c.c. of the filtrate are added 2 c.c. of solution (2). It is heated as before, and after cooling 2 c.c. of 75 p.c. hydrochloric acid are added, and the liquid is titrated with $\frac{N}{400}$ thiosulphate.

TABLE FOR 0·2 C.C. OF BLOOD.

Glucose		Glucose	
mg.	A-B	mg.	A-B
0·03	→ 0·12	0·22	→ 2·61
0·04	0·25	0·23	2·74
0·05	0·38	0·24	2·86
0·06	0·50	0·25	2·99
0·07	0·62	0·26	3·11
0·08	0·73	0·27	3·24
0·09	0·86	0·28	3·36
0·10	0·99	0·29	3·49
0·11	1·13	0·30	3·61
0·12	1·26	0·31	3·74
0·13	1·39	0·32	3·87
0·14	1·53	0·33	3·99
0·15	1·67	0·34	4·12
0·16	1·80	0·35	4·24
0·17	1·94	0·36	4·37
0·18	2·07	0·37	4·49
0·19	2·22	0·38	4·62
0·20	2·35	0·39	4·74
0·21	2·49	0·40	4·87

TABLE XXXII.—Amounts of Glucose corresponding to Copper. Cuprous Titration.
5 c.c. reagent+5 c.c. sugar solution.

Copper reduced	Micro burner 2½ minutes		Water bath 15 minutes		0·005 N-iodine required to oxidise cuprous oxide	Glucose in blood	
	Glucose	Glucose in blood	Glucose	Glucose in blood		Micro burner 2½ minutes	Water bath 15 minutes
mg.	mg.	p.c.	mg.	p.c.	c.c.	p.c.	p.c.
0·1	0·070	0·014	0·07	0·014	0·5	0·020	0·020
0·2	0·133	0·026	0·13	0·026	1·0	0·040	0·040
0·3	0·186	0·037	0·18	0·037	1·5	0·056	0·056
0·4	0·235	0·047	0·24	0·047	2·0	0·067	0·067
0·5	0·278	0·055	0·29	0·058	2·5	0·082	0·083
0·6	0·326	0·065	0·33	0·066	3·0	0·100	0·096
0·7	0·374	0·075	0·37	0·074	3·5	0·114	0·109
0·8	0·415	0·083	0·41	0·082	4·0	0·130	0·122
0·9	0·465	0·093	0·45	0·090	4·5	0·145	0·135
1·0	0·515	0·103	0·50	0·100	5·0	0·160	0·148
1·1	0·564	0·113	0·54	0·108	5·5	0·175	0·162
1·2	0·614	0·123	0·58	0·116	6·0	0·189	0·176
1·3	0·664	0·133	0·62	0·124	6·5	0·202	0·188
1·4	0·711	0·142	0·66	0·132	7·0	0·217	0·200
1·5	0·758	0·151	0·70	0·140	7·5	0·232	0·214
1·6	0·804	0·161	0·75	0·150	8·0	0·245	0·227
1·7	0·852	0·170	0·79	0·158	8·5	0·259	0·243
1·8	0·900	0·180	0·83	0·166	9·0	0·274	0·255
1·9	0·945	0·189	0·88	0·176	9·5	0·287	0·268
2·0	0·99	0·198	0·91	0·182	10·0	0·300	0·280
2·2	1·077	0·215	1·00	0·200	10·5	0·315	0·292
2·4	1·17	0·234	1·08	0·216	11·0	0·332	0·305
2·6	1·255	0·251	1·17	0·234	11·5	0·349	0·317
2·8	1·34	0·268	1·25	0·250	12·0	0·365	0·329
3·0	1·428	0·285	1·33	0·266	12·5	0·380	0·342
3·2	1·515	0·303	1·42	0·284	13·0	0·396	0·356
3·4	1·61	0·322	1·49	0·298	13·5	0·413	0·369
3·6	1·714	0·343	1·56	0·312	14·0	0·430	0·383
3·8	1·815	0·363	1·63	0·326	14·5	0·449	0·397
4·0	1·914	0·383	1·71	0·342	15·0	0·457	0·410
4·2	2·02	0·404	1·80	0·360			
4·4	2·12	0·424	1·89	0·378			
4·6	2·24	0·448	1·98	0·396			
4·8			2·06	0·412			

inhibits the reaction of cupric salts with soluble iodide. The reaction may thus be caused to take place to completion in either direction, and the determination by iodometric titration of either the cupric or the cuprous copper in a mixture of the two forms can be carried out. The authors prefer the latter method, which is here given.

Solutions required.—(1) Micro carbonate-tartaric acid reagent. Final concentration :

	Grams per litre
0·02 M copper sulphate (cryst.)	5·0
0·05 „ tartaric acid	7·5
0·4 „ sodium carbonate (anhyd.)	40·0
0·02 NI ₂ potassium	iodide . . . 10·0
	iodate . . . 0·7
0·1 M „ oxalate	18·4

Dissolve the carbonate in about 400 c.c. of warm water, and into this pour with stirring the copper sulphate and tartaric acid dissolved in about 150 c.c. of water. Dissolve the iodate, iodide, and oxalate in about 250 c.c. of water, rinse into the alkaline copper solution, cool, and dilute to one litre.

- (2) N-sulphuric acid.
- (3) 0·005N sodium thiosulphate solution.

Method.—To a measured volume of oxalate blood (1 c.c. is enough) add seven volumes of

THE METHOD OF SHAFFER AND HARTMANN
(J. Biol. Chem. 1920, 45, 365).

Principle.—The method is similar to that of Maclean. The reversible reaction



is applied to the determination of the mixture of cuprous and residual cupric compounds resulting from the action of the reducing sugar upon alkaline copper solutions. The direction in which this reversible reaction will proceed depends upon the concentration of the active substances. For the complete conversion of cupric to cuprous salt the concentration of iodide must be high. On the other hand, for the complete oxidation of the cuprous salts by the iodine, the concentration of the cupric and iodide ions must be very low; this can be attained by great dilution, as is the case in the method of Maclean. Shaffer and Hartmann have introduced for this purpose the use of alkali oxalate, the presence of which completely

water and allow to lake. Add one volume of 10 per cent. sodium tungstate, and one volume of $\frac{2}{3}N$ sulphuric acid. Or more conveniently, as recommended by Haden (J. Biol. Chem. 1923, 56, 467), and carried out at the National Institute for Medical Research, add 1 c.c. of blood directly to 8 c.c. of $N/12$ sulphuric acid, before putting in the sodium tungstate. Stopper and shake; filter after five minutes.

Measure into a large test-tube 5 c.c. of the carbonate-tartaric-acid reagent, add to it an equal volume of the sugar filtrate. Cover the tube, and either boil for $2\frac{1}{2}$ minutes over a small

2 c.c. of reagent+2 c.c. sugar solution			10 c.c. of reagent+10 c.c. of sugar solution		
Heated 10 minutes in boiling water bath			Heated 20 minutes in boiling water bath		
Copper reduced	Glucose	Glucose in blood	Copper reduced	Glucose	Glucose in blood
mg.	mg.	p.c.	mg.	mg.	p.c.
0.1	0.083	0.042	0.4	0.38	0.038
0.2	0.124	0.062	0.6	0.47	0.047
0.3	0.165	0.083	0.8	0.52	0.052
0.4	0.206	0.103	1.0	0.62	0.062
0.5	0.247	0.124	1.5	0.84	0.084
0.6	0.288	0.144	2.0	1.03	0.103
0.7	0.329	0.165	2.5	1.25	0.125
0.8	0.370	0.185	3.0	1.45	0.145
0.9	0.410	0.205	3.5	1.66	0.166
1.0	0.452	0.226	4.0	1.87	0.187
1.1	0.493	0.247	4.5	2.07	0.207
1.2	0.534	0.267	5.0	2.27	0.227
1.3	0.575	0.288	5.5	2.48	0.248
1.4	0.614	0.307	6.0	2.69	0.269
1.5	0.656	0.328	6.5	2.90	0.290
1.6	0.698	0.349	7.0	3.10	0.310
1.7	0.739	0.370	7.5	3.30	0.330
1.8	0.780	0.390	8.0	3.50	0.350
1.9	0.821	0.411	9.0	3.92	0.392
2.0	0.862	0.431	10.0	4.32	0.432

flame, or place in a boiling water bath for 15 minutes. Cool for several minutes under the tap. Add 5 c.c. of N sulphuric acid, and after about 1 minute titrate with $0.005N$ thiosulphate, using starch as an indicator.

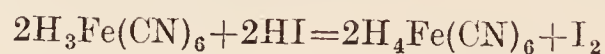
A blank titration on the reagent is determined after heating with an equal volume of water. The value of the blank does not change during at least several months, and, therefore, need be determined only occasionally. The difference between the blank, and a titration of a determination represents the iodine required for the oxidation of the reduced copper, and the corresponding amount of the sugar is ascertained from the table. (1 c.c. of $0.005N$ thiosulphate \equiv 0.318 mg. copper.)

When 10 c.c. or 2 c.c. of the blood filtrate and reagent are used, a proportionate amount of acid is taken, and the corresponding table is used for the calculation.

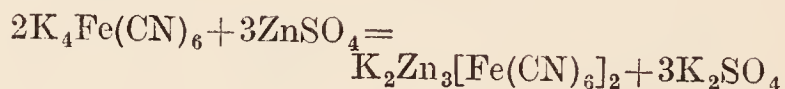
These directions are applicable to blood containing not more than 0.4 p.c. of glucose, for higher concentrations the blood filtrate is diluted, or a smaller amount (and water) is taken for the determination.

THE METHOD OF HAGEDORN AND JENSEN (Biochem. Zeitsch. 1923, 135, 46).

Principle.—After removal of the proteins the sugar of the blood is oxidised by a known volume of a standard solution of potassium ferricyanide in excess. The unused potassium ferricyanide is estimated by treatment with potassium iodide in the presence of zinc salts, when iodine is liberated:



This reaction is reversible, but proceeds quantitatively to the formation of iodine, and ferrocyanide if the latter is removed from the reaction mixture by precipitation as the zinc compound



The amount of iodine present is determined by titration with thiosulphate solution.

Solutions required.—(1) An alkaline $0.005 N$ -solution of potassium ferricyanide.

This is made by dissolving 1.65 grms. of potassium ferricyanide and 10.6 grms. of anhydrous sodium carbonate in water, and making up to 1 litre. The solution should be protected from light, but will keep in a black bottle for two months. The purity of the reagents is of the highest importance; the sodium carbonate should be recrystallised, and ignited in a platinum crucible.

The pure commercial potassium ferricyanide should be washed in cold water, dissolved in hot water, and filtered through a filter previously washed with hot water. The filtrate should be received into a dish floating on ice-cold water. The crystals formed should be again carefully washed, dissolved, and recrystallised. The whole of these processes should be carried out in a dark room.

(2) The potassium-iodide zinc sulphate-sodium-chloride solution.

This consists of:

Potassium iodide (free from iodate) .	5 grms.
Zinc sulphate	10 "
Sodium chloride	50 "
Water to	200 c.c.

All these reagents must be iron free. The solution is not absolutely stable, for this reason it is preferable to make it without the potassium iodide, and to add this to small portions as required.

(3) A 3 p.c. solution of acetic acid, which must be iron free.

(4) Starch solution: 1 gm. of soluble starch is dissolved in 100 c.c. of a saturated solution of sodium chloride.

(5) $0.005N$ sodium thiosulphate solution.

0.7 gm. sodium thiosulphate is dissolved in 1000 c.c. of water. This roughly made solution is standardised by a potassium iodate solution accurately prepared by dissolving 0.3566 grms. of pure anhydrous potassium iodate in water, and making up to 2 litres.

(6) The protein precipitating solutions: $0.1N$ sodium hydroxide and 0.45 p.c. zinc sulphate.

It is essential that all these reagents should be of the highest degree of purity.

Method.—Into a test-tube of about 15×150 mm. capacity are put 1 c.c. of $0.1N$ sodium

hydroxide, and 5 c.c. of 0.45 p.c. zinc sulphate. A precipitate of zinc hydroxide occurs, the zinc sulphate is in excess, so that the liquid does not become alkaline, even if the quantities are roughly measured. 0.1 c.c. of blood, measured with a capillary pipette, is blown into the zinc hydroxide, and the pipette is twice washed out with the mixture. The test-tube is then heated in a boiling water bath for 3 minutes. The liquid is then filtered through washed, and still wet, cotton wool, not too tightly packed, and the residue is washed twice with 3 c.c. of water. Exactly 2 c.c. of the alkaline ferricyanide solution are added, and the liquid is heated in the boiling water bath for 15 minutes. 3 c.c. of the potassium iodide solution, and 2 c.c. of 3 per cent. acetic acid are

added. The liquid is then titrated with the thiosulphate solution, which is run in from a microburette, the starch solution being used as an indicator.

Calculation.—The volume in c.c. of thio-sulphate used, multiplied by its factor, is subtracted from 2.00 (the volume of potassium ferricyanide taken). This number (since the ferricyanide and thiosulphate are both 0.005*N*) represents the ferricyanide used to oxidise the sugar. The corresponding percentage of blood sugar is found from the table.

In all reduction methods for sugar estimation the oxidation mixture is liable to undergo auto-reduction; one of the causes of this is the presence of micro-organisms. For this reason freshly distilled water should be used, and a

TABLE XXXIII.

c.c. *N*/200 sodium thiosulphate—mg. glucose.

	0	1	2	3	4	5	6	7	8	9
0.0	0.385	0.382	0.379	0.376	0.373	0.370	0.367	0.364	0.361	0.358
0.1	0.355	0.352	0.350	0.348	0.345	0.343	0.341	0.338	0.336	0.333
0.2	0.331	0.329	0.327	0.325	0.323	0.321	0.318	0.316	0.314	0.312
0.3	0.310	0.308	0.306	0.304	0.302	0.300	0.298	0.296	0.294	0.292
0.4	0.290	0.288	0.286	0.284	0.282	0.280	0.278	0.276	0.274	0.272
0.5	0.270	0.268	0.266	0.264	0.262	0.260	0.259	0.257	0.255	0.253
0.6	0.251	0.249	0.247	0.245	0.243	0.241	0.240	0.238	0.236	0.234
0.7	0.232	0.230	0.228	0.226	0.224	0.222	0.221	0.219	0.217	0.215
0.8	0.213	0.211	0.209	0.208	0.206	0.204	0.202	0.200	0.199	0.197
0.9	0.195	0.193	0.191	0.190	0.188	0.186	0.184	0.182	0.181	0.179
1.0	0.177	0.175	0.173	0.172	0.170	0.168	0.166	0.164	0.163	0.161
1.1	0.159	0.157	0.155	0.154	0.152	0.150	0.148	0.146	0.145	0.143
1.2	0.141	0.139	0.138	0.136	0.134	0.132	0.131	0.129	0.127	0.125
1.3	0.124	0.122	0.120	0.119	0.117	0.115	0.113	0.111	0.110	0.108
1.4	0.106	0.104	0.102	0.101	0.099	0.097	0.095	0.093	0.092	0.090
1.5	0.088	0.086	0.084	0.083	0.081	0.079	0.077	0.075	0.074	0.072
1.6	0.070	0.068	0.066	0.065	0.063	0.061	0.059	0.057	0.056	0.054
1.7	0.052	0.050	0.048	0.047	0.045	0.043	0.041	0.039	0.038	0.036
1.8	0.034	0.032	0.031	0.029	0.027	0.025	0.024	0.022	0.020	0.019
1.9	0.017	0.015	0.014	0.012	0.010	0.008	0.007	0.005	0.003	0.002

blank determination with the reagents should be made. The value of the blank is subtracted from the sugar value found.

The numbers inside the double lines of the table give mgs. of glucose per cent. The first row of vertical figures gives the volume in c.c. to the first place of decimals of the *N*/200 thiosulphate used. The top row of figures gives the second decimal place in this volume. Example: if 1.43 c.c. of *N*/200 thiosulphate are used in the sugar determination, this is equivalent to 0.101 mg. per cent. of glucose. From this must be subtracted the value of the blank, if for this 1.95 c.c. of thiosulphate are required, this is equivalent to 0.008 mg. glucose. The glucose value for the blood is therefore 0.101–0.008 mg. p.c. If 2 c.c. of thiosulphate are used the glucose is 0, and if 0 c.c. are required the glucose may be 0.385, or any value above this.

Other methods of estimating the blood sugar in use are those of Benedict (Lewis and Benedict, *J. Biol. Chem.* 1915 20, 61; 1918, 34, 203; and Bang, *Der Blutzucker*, Wiesbaden, 1913).

A colorimetric method which seems likely to be useful has been devised in the department

of Biochemistry of the University of Birmingham and worked out by Paton (*Bio-Chem. J.* 1924, 18, 965). It is an adaptation of the method of Sumner (*J. Biol. Chem.* 1921, 47–48, 5) for the colorimetric estimation of sugar in urine, and depends upon the red colour produced by glucose with 3–5 dinitrosalicylic acid. The blood sugar filtrate, prepared according to the method of Maclean, after treatment with the sodium salt of dinitrosalicylic acid, is compared colorimetrically with a standard solution of glucose.

H. W.

INSULIN AS A MEANS OF CONTROLLING BLOOD SUGAR IN DIABETES MELLITUS.

After von Mering and Minkowski (*Centralbl. f. klin. Med.* 1889, 10, 393) had shown that extirpation of the pancreas produces glycosuria in the dog, and subsequently, when it was established that the mechanism which regulates sugar metabolism is humoral in character, attempts were made to localize the secretion and to obtain a preparation which on administration should lower the blood-sugar and thus prevent the glycosuria of diabetes. The pancreas is a composite gland; it consists

of an exocrine portion which secretes the enzyme-containing pancreatic juice through the pancreatic duct into the intestine, and of an endocrine part, the so-called islets of Langerhans which were ultimately shown to furnish a secretion to the blood, and thereby regulate its sugar-content. Attempts to obtain this latter secretion which should be capable of temporarily conferring on a diabetic the power of utilising sugar, possessed by the normal individual, were for a long time unsuccessful. The reason is that *insulin*, the active principle of the islets of Langerhans, is destroyed by the proteolytic ferment of pancreatic juice, and unless special precautions are taken, this destruction occurs when the whole pancreas is extracted, since in it both secretory tissues are intimately mixed. This association of two tissues in one gland, which so long delayed progress, still causes one of the main difficulties in the manufacture of insulin.

An active extract of islet tissue was first obtained by Banting and Best (J. lab. and clin. Med. 1922, 7, 251). They ligatured the pancreatic duct in dogs, so as to cause degeneration of the exocrine portion of the gland. When this process was complete the animal was killed; its pancreas then yielded an extract which caused diminution of blood-sugar when injected into rabbits. The same authors obtained an active extract from the pancreas of foetal calves before the fifth month of gestation; at this stage the internal secretion is already active, while the external one has not yet been formed. In certain fishes (e.g. *Lophius piscatorius*) the islet tissue forms isolated masses, and as long ago as 1907, Rennie and Frazer attempted to treat diabetes with these organs, but without success, probably because they administered them by the mouth, so that the active principle was destroyed by the proteolytic enzymes of the patient. Macleod (J. metabol. Research, 1922, 2, 149) showed that an extract of the islets of fishes is active, when administered hypodermically.

However important scientifically, these methods are of no practical importance for manufacturing insulin, not even the last-named. Although 20–30 times as much insulin may be obtained from fish islet tissue as from mammalian pancreas, and 1 grm. of the islet tissue may yield 40 clinical doses of insulin, the amount of this tissue in fishes is so small that the difficulty of collecting it is excessive. In practice we are at present restricted to the whole pancreas of animals from abattoirs. It should, however, be noted that substances capable of lowering blood-sugar are obtainable from sources other than the pancreas; for these Collip has suggested the name *glucokinins*; whether any of them are identical with insulin is doubtful. Substances of this kind have been obtained from higher plants by Collip (J. Biol. Chem. 1923, 57, 65), and from yeast by Hutchinson, Smith and Winter (Bio-Chem. J. 1923, 17, 683). Perhaps the observations of Best, Smith and Scott (J. Biol. Chem. 1924, 59, xxx.) may prove more useful; they found a blood-sugar-reducing substance in the brain, heart and skeletal muscle, blood, lung, liver, spleen, kidney, submaxillary, thyroid and thymus glands of dogs.

The first extracts to be used clinically were made from the whole pancreas by the method of Collip (J. Biol. Chem. 1923, 56, xl.–xli.). Soon after death of the pancreas the trypsinogen becomes activated, but proteolytic action can be stopped by dropping the minced pancreas into alcohol of such strength that the trypsin is precipitated and the insulin is dissolved. This is the basis of all present methods of extracting insulin. Various workers have recommended acidification of the alcohol in order to counteract tryptic action still further, but since insulin is readily adsorbed from acid solution by many substances, including proteins, Dudley and Starling (Bio-Chem. J. 1924, 18, 147) add sodium bicarbonate to the alcohol and obtain a much better yield. The purification of the extract was first carried out by Collip by fractional precipitation of the proteins with alcohol, to which Doisy, Somogyi and Shaffer (J. Biol. Chem. 1923, 55, xxxi.; 1924, 60, 31) later added ammonium sulphate. These authors further affected considerable purification by utilising the slight solubility of insulin in water at its iso-electric point ($P_H=5.2$), as compared with its great solubility on either side of this point. Dudley (Biochem. J. 1923, 17, 376), also found a powerful means of purification in the precipitation of insulin by picric acid, and subsequent regeneration of the picrate by alcoholic hydrochloric acid.

All these improvements are utilised in the *large-scale manufacture*, which has been described by Carr (J. Soc. Chem. Ind. 1924, 43, 228T). The pancreas of the sheep, pig or ox is dissected free from fat and connective tissue, and is frozen; in this condition it can be kept for a considerable time without destruction of insulin. The frozen gland is finely minced at a low temperature, and is extracted with alcohol of 65–70 p.c.; the reaction is either made acid to $P_H 2.5$, by adding sulphuric acid, or is adjusted to $P_H 7.0$, following Dudley and Starling's bicarbonate method (see above). The alcoholic extract is cooled to -5° and filtered or centrifuged. It is then concentrated at a low temperature under diminished pressure to one-tenth of its original volume. The resulting aqueous solution is freed from fat and precipitated with ammonium sulphate; the precipitate is dissolved in water and reprecipitated by alcohol containing sulphuric acid. The crude insulin thus obtained is dissolved in water, and aqueous 1 p.c. picric acid is added. After filtering off and washing, the picrate is dissolved in 75 p.c. alcoholic normal hydrochloric acid, and the commercial insulin is thrown down by adding acetone. For further details Carr's paper, above referred to, should be consulted; it contains a flow-sheet of the process. Continued improvements in the yield have reduced the selling-price of insulin in one year from 25s. to 2s. 8d. per 10 doses (=100 units).

As an example of a *laboratory method*, the description by Dudley and Starling (Bio-Chem. J. 1924, 18, 147) may be quoted: One kilogram of fresh ox pancreas is minced into one litre of 95 p.c. spirit; 85 grn s. sodium bicarbonate are stirred into the mixture, which is then poured into the mincer and reminced; this procedure

is repeated a second time. The mixture is then allowed to stand with frequent stirring for two hours at room temperature, or if desired it may be kept in the cold room overnight. It is then poured on to a stout cloth, which is squeezed as thoroughly as possible in a suitable press. The turbid filtrate which has a P_H of about 7.5 is treated with $1\frac{1}{2}$ times its volume of 95 p.c. spirit and placed in the cold room (-3°) overnight. It is then filtered through a folded paper; 10 c.c. of glacial acetic acid are added to the filtrate, which is then evaporated *in vacuô*, in a water-bath at 40° – 45° . When the volume of the residue has reached about 150 c.c., the fat which has separated is removed by shaking out with light petroleum, and the aqueous layer is freed from traces of this solvent by a few minutes' distillation under the conditions described above. Four volumes of absolute alcohol are added to the aqueous solution, and after standing for about ten hours in the cold room, the alcoholic solution is carefully decanted from the precipitate which has formed and two volumes of absolute alcohol are added to it. After standing in the cold room for 12–14 hours the supernatant liquid is carefully decanted and the precipitate is washed into centrifuge tubes with absolute alcohol, washed with absolute alcohol and dry ether, and finally dried in a vacuum desiccator over sulphuric acid. The average yield of crude insulin by this process was 2.16 grms. and 412 rabbit units (see below) per kilo. of pancreas. This crude insulin may be purified as follows: It is dissolved in a small volume of water, and the flocculent, insoluble material is removed by centrifuging. The clear solution is then diluted with the requisite amount of water to give a 1.5 p.c. concentration of the original material, making no allowance for the insoluble material which has been removed. The P_H of the solution is then adjusted to about 5. This may be conveniently accomplished by adding acid or alkali (according to the original P_H) until a faint turbidity is produced, due to the formation of the 'isoelectric-point precipitate' (Doisy, Somogyi and Shaffer, *l.c.*). Half its volume of saturated aqueous picric acid is then added. After standing for a day or two the clear supernatant liquid is poured off. The lemon-yellow precipitate which has collected on the bottom of the beaker is rubbed up with a small quantity of water, and then $N/10$ sodium carbonate solution is added in small quantities at a time with constant stirring until a clear, or nearly clear, dark brown solution is obtained. As soon as addition of sodium carbonate solution fails to clarify the solution further, it is filtered through a folded filter paper, which is well washed with distilled water on completion of the filtration. This process should be carried out with all reasonable speed, and it is well to keep the temperature below 10° . The solution is then diluted to contain about 1.5 to 2 gm. of picrate per litre. The necessary volume is calculated on the assumption that the amount of picrate obtained is about one-twelfth the weight of the original crude insulin. An amount of $N/10$ HCl, equivalent to the Na_2CO_3 used, is then added to the well-stirred liquid. An immediate precipitation of the picrate

occurs. To each litre of solution is added 250 c.c. of saturated aqueous picric acid. After standing for a day or two the precipitate has again collected on the bottom of the beaker and the clear supernatant liquor is poured away. A solution containing 5 c.c. of saturated aqueous picric acid in 100 c.c. water is made. The picrate is rubbed up in a small quantity of this solution, and is then filtered on a Buchner funnel. After adequate washing with the dilute picric acid solution to remove sodium chloride, the moist picrate is transferred to a beaker and stirred with a solution of hydrochloric acid in 75 p.c. alcohol, prepared by mixing 25 c.c. 3*N* (aqueous) HCl with 75 c.c. of absolute alcohol. The picrate, after first forming thick, dark brown sticky drops, dissolves in this reagent, yielding a turbid, brown solution. It must be stirred until all the sticky drops have disappeared. The amount of the alcoholic-aqueous HCl reagent used is not important, but from 10–15 c.c. per gm. of picrate is an appropriate quantity. Pure acetone is then added rapidly until no further precipitate appears. From 10–20 volumes are necessary. The white flocculent precipitate of 'insulin hydrochloride' settles rapidly and is immediately filtered on a Buchner funnel, washed with acetone and finally with dry ether until perfectly free from picric acid. The funnel with its contents is quickly transferred to a vacuum desiccator and dried over sulphuric acid. This method may yield a preparation of which one rabbit unit weighs as little as 0.2 mg., whereas one rabbit unit of the crude insulin prepared by the sodium bicarbonate method weighed about 25 times as much. Although insulin picrate is practically insoluble in water and in absolute alcohol, it dissolves freely in mixtures of the two, so that it cannot be precipitated satisfactorily from aqueous solutions containing alcohol.

Physical and Chemical properties.—Since even the purest insulin preparations are mixtures, we are rather ignorant of the properties of the pure active principle. In many respects it behaves like a fairly complex peptide. It is readily soluble in water, except at its isoelectric point ($P_H=5.2$) and in strongly acid solution, *e.g.* N HCl, when a hydrochloride is precipitated from concentrated solution. It is soluble in 90 p.c. alcohol, except at the isoelectric point. It is precipitated by half-saturation with ammonium sulphate or sodium chloride, and by picric, phosphotungstic and trichloroacetic acids; it is insoluble in absolute alcohol. The active principle is readily adsorbed from faintly acid solution by kaolin, animal charcoal and a Berkefeld filter (*e.g.* $P_H=6.6$). It can, however, be filtered through a Berkefeld filter and sterilised without appreciable loss in faintly alkaline solution (*e.g.* $P_H=7.4$). It cannot be filtered through collodion and only dialyses very slowly, if at all. It is evidently a substance of high molecular weight.

For the behaviour of insulin towards Fehling's solution. see Knops-Niederhoff (J. Pharm. Belg. 1924, 6, 160; Pharm. J. 1924, 113, 45; Analyst, 1924, 49, 445).

The purest insulin prepared from ox pancreas gives a biuret reaction, but according to Best and Macleod that prepared from the skate does

not. The purest insulin gives no reactions for tryptophan, tyrosine and phosphorus, but always gives Pauly's histidine reaction and tests for organic sulphur. Insulin is destroyed by pepsin, by trypsin and by alkali; it is slightly more stable in acid solution. Thus at 37° it is almost completely destroyed by *N*/10 sodium hydroxide in 1½ hour; at 100° it is destroyed in 10 minutes in *N*/10 sodium carbonate, and also in neutral solution, but in *N*/10 acid some still remains after heating to 100° for one or two hours.

For the chemical reactions of insulin, see Best and MacLeod (Amer. J. Physiol. 1923, 63, 390; Chem. Soc. Abstr. 1924, 126, i. 898).

Physiological properties and standardisation.—The hypodermic injection of insulin causes a rapid fall of blood-sugar, which fall is used therapeutically in human diabetes, and for pharmacological assay in rabbits. The amount of glucose in normal human blood is about 0.1 p.c.; in the diabetic it may rise to about 0.2 p.c., and then overflows through the kidney, causing glycosuria. Exactly how insulin causes the diminution of the blood-sugar is not known; the substance is extremely active in this respect, since 0.1 mg. of the most active preparation may cause 3 grms. of sugar to disappear in 2 hours. Insulin also causes disappearance of aceto-acetic acid.

The drug is tested by injection into rabbits, which have fasted for 24 hours so as to reduce the glycogen content of the liver. The (original Toronto) rabbit unit is the amount necessary, when injected subcutaneously, to lower the blood-sugar of a 2-kilo. rabbit from its normal value of about 0.1 p.c. to 0.045 p.c. within 4 hours. This low blood-sugar level causes convulsions in the rabbit, and an overdose of insulin in a diabetic may also produce severe symptoms; they are promptly relieved by taking sugar by the mouth. The above rabbit unit was found to be too large for clinical purposes, and a clinical unit is taken as one-third of a rabbit unit. The amount of insulin required to lower the blood-sugar to 0.045 p.c. is by no means proportional to the weight of the rabbit; rabbits of the same weight moreover vary in sensitiveness, and the International Conference on Biological Standards, held at Edinburgh in 1923, agreed that a unit should, if possible, be fixed in terms of a stable standard preparation, to be prepared for the purpose. It is one of the drawbacks of insulin that it must be administered hypodermically (usually twice a day) in order to avoid destruction by digestive enzymes.

For a general account of insulin, see The Insulin Treatment of Diabetes Mellitus, by P. J. Cammidge, 2nd ed., Edinburgh, 1924, pp. viii.+216. This book contains no literature references, which will, however, be found, in the shape of a bibliography, in a review of the subject by H. Simonnet in the Bulletin de la Société de chimie biologique, January, 1924, 6, pp. 44–112. G. B.

SUGAR BEET GUM *v.* GUMS.

SUGAR CANE WAX *v.* WAXES.

SUGAR OF LEAD. *Lead acetate* (*v.* ACETIC ACID).

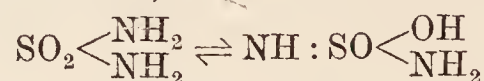
SUINE. A butter substitute made from pigs' fat (*v.* MARGARINE).

SULFAMINOL *v.* SYNTHETIC DRUGS.

SULFOID. Trade name for a preparation of colloidal sulphur and albumen.

SULFOSOT *v.* SYNTHETIC DRUGS.

SULPHAMIDE absorbs 1.4 molecular proportions of dry ammonia at +20°, 3.0 molecular proportions at 0°, and 5.4 molecular proportions at –20°. The product so formed has an electrical conductivity about 150 times that of a 4*N*-aqueous solution of sulphamide. Furthermore, a 4*N*-aqueous solution of sulphamide-ammonia has a conductivity twenty-five times that of a 4*N*-solution of ammonia alone. It is therefore suggested that sulphamide can also exist in an aci-form, thus



just as in the case of carbamide. The sodium, lithium, potassium, barium, and calcium salts are described as colourless, non-hygroscopic crystals, whilst the cupritetrammine and cupriethylenediamine salts were obtained as blue crystalline solids. *Benzylidenesulphamide* $\text{NH}_2 \cdot \text{SO}_2 \cdot \text{N} : \text{CHPh}$, was obtained by the elimination of water from benzaldehyde and sulphamide by means of anhydrous copper sulphate. It forms needles, m.p. 135°, soluble in methyl alcohol, ethyl alcohol, and benzene. *Monochloro-sulphamide*, prepared by the action of hypochlorous acid on sulphamide, melts at 66° with decomposition, and is easily soluble in water, alcohol, or chloroform. Details are given of an improved method of preparation of sulphamide from sulphuryl fluoride (Wilhelm Traube and Emil Reubke, Ber. 1923, 56, [B] 1656–1663; J. Chem. Soc. Abstr. 1923, 124, ii. 630).

SULPHAMMONIUM. The various forms of sulphur dissolve in liquid ammonia forming a purple solution, which, according to Moissan, contains a definite compound, stable up to 90°, which he terms *sulphammonium*. It gives a characteristic absorption spectrum and reacts with iodine and a number of metals and salts forming coloured substances decomposing at the ordinary temperature and pressure (Moissan, Bull. Soc. chim. 1902, [iii.] 27, 652).

SULPHANILIC ACID (*Aniline p-sulphonic acid*) $\text{C}_6\text{H}_4 \cdot \text{NH}_2 \cdot \text{HSO}_3$, or $\text{C}_6\text{H}_4 < \begin{matrix} \text{SO}_3 \\ \text{NH}_3 \end{matrix} >$, or

$\text{NH}_2 \text{—} \text{C}_6\text{H}_4 \text{—} \text{SO}_3\text{H}$ is formed by heating aniline *p*-phenol sulphonate, or by heating aniline with concentrated sulphuric acid, or aniline ethyl sulphate to 200° (Limpricht, Annalen, 1875, 177, 80); the nitration products of benzene sulphonic acid, when reduced with ammonium hydroxide and hydrogen sulphide, yield the three aminosulphonic acids, which may be separated mechanically after recrystallisation. The light crystals of the *m*-acid rise to the surface, and may be removed from the others by washing. The residue is heated to 110°–120° when the *p*-acid becomes powdered and may be separated by passing through a sieve (Franklin, Amer. Chem. J. 1898, 20, 457).

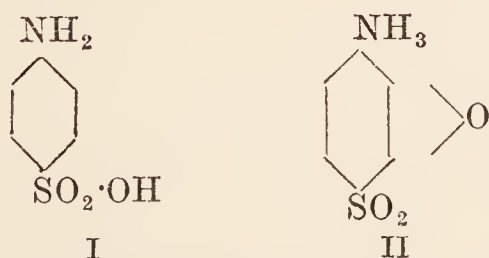
Sulphanilic acid may be prepared by heating 28 parts of chlorobenzene-*p*-sulphonic acid with 370 of 25 p.c. ammonia solution, and 5 of cupric chloride for 12 hours to 170° in a closed vessel. The mass is then mixed with sodium carbonate,

the ammonia is distilled off, the residue filtered and concentrated, when the sodium salt of sulphanilic acid separates (Bloxam, D. R. P. 205150; J. Soc. Chem. Ind. 1908, 1147). The acid may also be obtained by the action of hot strong acids or alkalis on acetylaniline *p*-sulphonamide (Gelmo, J. pr. Chem. 1908, [ii.] 77, 369), and by other methods (Gerhardt, Annalen, 1846, 60, 310; Buckton and Hofmann, *ibid.* 1856, 100, 163; Pratesi, Ber. 1871, 4, 970; Kopp, *ibid.* 978; Bamberger and Kunz, *ibid.* 1897, 30, 2277; Wenghöffer, J. pr. Chem. 1877, [ii.] 16, 454; Wohlfahrt, *ibid.* 1902, 66, 551; Cohn and Springer, Monatsh. 1903, 24, 87; Bouchetal, Bull. Soc. chim. 1904, [iii.] 31, 24).

On the large scale it is prepared by heating aniline acid sulphate $C_6H_5 \cdot NH_2 \cdot H_2SO_4$ in a shallow iron pan at 230° – 235° so long as sulphur dioxide is evolved.

Sulphanilic acid forms a monohydrate and a dihydrate. The stable solid in contact with saturated solutions is dihydrate from 0° to 21° , monohydrate from 21° to 40° , and anhydrous acid from 40° upwards (Philip, Chem. Soc. Trans. 1913, 284). The dihydrate is strongly efflorescent, and on losing its water at the ordinary temperature passes directly into the anhydrous acid. The latter may be obtained by crystallisation not only from hot water, but also from fuming sulphuric acid (Laar, Ber. 1881, 14, 1933). It chars when heated to 280° – 300° . It acts as a monobasic acid (Astruc, Compt. rend. 1900, 130, 1563), yields aniline when fused with caustic potash, and when the barium salt is treated with bromine water, it forms tribromaniline and barium dibromoanilinesulphonate. When oxidised with chromic acid it yields quinone (Schrader, Ber. 1875, 8, 759; Limpricht, *ibid.* 1885, 18, 1419; Laar, J. pr. Chem. 1879, [ii.] 20, 242).

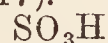
Sulphanilic acid behaves as a monobasic acid in alkaline solutions and is neutral in its influence on the inversion of sucrose by hydrochloric acid. On these grounds Waterman (Proc. K. Akad. Wetensch. Amsterdam, 1918, 20, 581) assigns the constitution I to sulphanilic acid in alkaline solution, and constitution II in acid solution.



Sulphanilic acid forms salts with the alkali metals, also with barium, copper, silver, and cerium (Gerhardt, *l.c.*; Laar, *l.c.*; Morgan and Cahen, Chem. Soc. Trans. 1907, 477). On pouring a mixture of sodium sulphanilate and sodium nitrite in aqueous solution into dilute sulphuric acid there is formed *benzene-diazonium sulphonc acid* $C_6H_4 \langle \begin{smallmatrix} N_2 \\ SO_3 \end{smallmatrix} \rangle$, which is important in the preparation of azo dyes, such as heli-anthine. Finely powdered dry sodium sulphanilate reacts with acetic anhydride forming *sodium acetylaniline-p-sulphonate*, which, with concentrated sulphuric acid, yields the free acid $NHAc \cdot C_6H_4 \cdot SO_3H$. The sodium acetyl salt

treated with phosphorus pentachloride and then with cold water yields the corresponding *sulphonyl chloride* $NHAc \cdot C_6H_4 \cdot SO_2Cl$, m.p. 149° (Schroeter, Ber. 1906, 39, 1559).

When 46.2 grms. of sodium *p*-sulphanilate is heated with 1 litre of water, 18 c.c. hydrochloric acid, and 54 grms. of tetramethyldiaminodiphenylcarbinol, on a water-bath for 6 hours to 80° – 90° , equal quantities of the following substances are obtained: (1) a yellow crystalline compound dyeing tannin-mordanted cotton yellow, similar to auramine; (2) a sulphonated leuco base, converted by lead peroxide into a green dyestuff for wool, decolorised by alkalis; (3) a substance soluble in water, which does not yield a dyestuff on oxidation; (4) hexamethyl-triaminotriphenylmethane (crystal violet). *m*-Sulphanilic acid treated similarly (but in different proportions), yields as chief product a sulphonated leuco base, which, on oxidation, yields a violet dyestuff turned green by caustic soda. If the leuco base is diazotised, boiled with water, and then oxidised, it yields a green dyestuff, reddened by alkalis; but if the diazo compound is boiled with alcohol and the product oxidised with lead peroxide, it forms a dyestuff which colours wool bluish-green shades remarkably fast to caustic soda (Suais, Bull. Soc. chim. 1897, [iii.] 17, 517).



Metanilic acid $NH_2 \text{C}_6H_4$ is prepared by sulphonating nitrobenzene and reducing the nitrobenzene sulphonic acid with iron (Paul, Zeitsch. angew. chem. 1896, 9, 686).

For the preparation of *aniline-o-sulphonic acid*, see Obermiller, D. R. P. 281176.

SULPHARSENOL. A compound of arsenobenzol glycol and sodium acid sulphite, used as a substitute for neosalvarsan.

SULPHATASE. An enzyme found in *Aspergillus oryzae*. Incubated at $37^\circ C$. with solutions of potassium phenyl sulphate, it caused a marked hydrolysis, amounting in sixteen days to 13.6 p.c. of the substrate (C. Neuberg, Biochem. Zeitsch. 1923, 140, 295–298).

SULPHAZIDES may be prepared by the action of sulphurous acid upon the acid solution of diazo salts, or by passing nitrous acid into or adding potassium nitrite to an ice-cooled solution of the diazo salt in alcohol saturated with sulphurous acid (Limpricht, Ber. 1887, 20, 1238). According to Eng. Pat. 12872, 1900, a much better yield is obtained by diazotising an aromatic amine in hydrochloric acid solution, mixing this with sodium bisulphite and adding the diazo sulphite thus formed to an alcoholic solution of sulphurous acid (J. Soc. Chem. Ind. 1000, 893).

Phenylbenzenesulphazide



forms white leaflets, m.p. 148° – 150° .

o-Tolyltoluenesulphazide



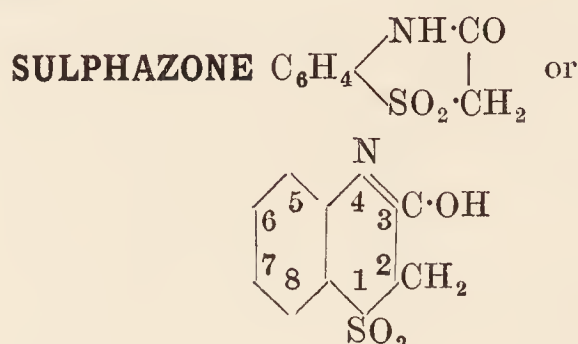
forms white lustrous needles, m.p. 140° – 142° (decomp.); the *p*-tolyl-derivative has m.p. 140° .

Nitro derivatives of these compounds are described by Limpricht (*l.c.*).

When the sulphazides are heated with baryta, or with soda solution, or with alcoholic soda, they

are decomposed, yielding the corresponding sulphinic acid, nitrogen, and an aromatic hydrocarbon.

Similarly, nitrosulphinic acids and nitrohydrocarbons are formed from the nitrosulphazides.



Dark brown leaflets, m.p. 207° – 208° . Soluble in sodium hydroxide: no coloration with ferric chloride. Is obtained in about 95 p.c. yield by treatment of *o*-nitrophenylsulphonyl-acetic acid $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, m.p. 173° – 174° , with iron in neutral solution or suspension, preferably in presence of a neutral salt, and subsequent addition of excess of a mineral acid. Claasz's process (Ber. 1912, 45, 747; D. R. P. 256342), by which the substance was first made, consists in reducing the *o*-nitrophenylsulphonyl-acetic acid with zinc-dust and hot acetic acid, gives a yield of about 77 p.c. (Farbwerke vorm. Meister, Lucius and Brüning, D. R. P. 269428).

The hydrogen atoms in the group $\text{SO}_2\cdot\text{CH}_2\cdot\text{CO}$ are very reactive and dyes are obtained by condensing sulphazone with diazonium salts in alkaline solutions, dyeing wool or silk brownish-yellow or golden-yellow colours. For other derivatives, see Claasz (Ber. 1916, 49, 350). For dyes derived from sulphazone, see Herzog (Ber. 1918, 51, 516).

SULPHIDE DYES.

Historical summary.—Sulphur enters into the composition of many important organic colouring matters of widely different properties and mode of application (*v.* METHYLENE BLUE, PRIMULINE, &c.), but the group of dyes comprised under the above heading is distinguished by the dyeing process employed in fixing these compounds on the textile fibres, usually cotton. The sulphide dyes are soluble with reduction in aqueous solutions of the alkali sulphides giving rise to leuco derivatives which have a considerable affinity for the cotton fibre. After absorption by the cotton these leuco compounds are oxidised *in situ* to the insoluble dye, either by air or by chemical agents. In this behaviour the sulphide colours somewhat resemble indigotin, thioindigo, and other vat dyes (*v.* VAT DYES, &c.), and proposals have been made for employing these colours in the vat-dyeing processes (D. R. PP. 146797, 200391).

The earliest experiments in this field of tinctorial chemistry were made by Troost in 1861, who reduced a crude mixture of 1 : 5- and 1 : 8-dinitronaphthalenes with sodium sulphide and other reducing agents, and obtained coloured products giving red, violet, and blue shades on the textile fibres (J. 1861, 958; *cf.* Fr. Pat. 244885). But although these experiments indicated the influence of sulphur in the conversion of organic compounds into colouring matters, the substances produced met with no

success as dyes. The first discovery of technical importance was embodied in a patent taken out by Croissant and Bretonnière (Eng. Pat. 1489, 1873; Fr. Pat. 98915; *cf.* Bull. Soc. Ind. Mulhouse, 1874, 468), in which these chemists showed that a very heterogeneous collection of organic materials were capable of yielding dyes when heated with alkali sulphides and polysulphides. The materials enumerated in the patent are in most cases products of the vital activities of animal and vegetable life, together with certain waste products of manufacture, among which the following may be mentioned: wood, sawdust, humus, vegetable detritus, lichens, mosses, bran, farina, gluten, starch, sucrose, glucose, cellulose, paper and cotton waste, tannin, gallic acid, gelatin, casein, albumin, blood, horn, feathers, animal excrement, the organic acids and their salts, aloes, resins, gums, gum-resins, and soot.

Two modes of interaction are distinguishable in the patent. In one process aloes are warmed with an aqueous solution of sodium polysulphide when a dye is produced, dyeing cotton in lilac and grey shades. The patentees state that this dye is an additive product, the sulphur being introduced into the molecule without replacement of hydrogen in the form of hydrogen sulphide.

In the second process, which is by far the more widely applicable, the organic matter is heated with alkali polysulphides at temperatures above 100° and approaching 300° . Substitution occurs, sulphur being introduced into the molecule while hydrogen sulphide is evolved. The products dye in various shades of brown, and the patentees' experiments indicated that the higher the temperature of heating the darker was the shade of colour produced.

In spite of the wide scope of the patent only one useful colour was obtained under it for about 20 years. This product was **Cachou de Laval**, a brown dye which was generally prepared by heating together sawdust, sodium sulphide, and sulphur (*v. infra*).

The next development in the sulphide dye industry occurred 20 years later, when Vidal found that certain aromatic nitro compounds were capable of yielding green, blue, brown, and even black dyes (**Vidal black**) when heated with alkali polysulphides. This discovery was the turning-point in the manufacture of sulphide colours, for from this time onward the attention of inventors was directed towards the production of these colours from definite coal-tar derivatives rather than from the ill-defined materials indicated in Croissant and Bretonnière's patent.

The compounds first utilised by Vidal for the production of brown and black sulphur dyes were the nitrated products of phenol and its homologues. Acyl derivatives of aromatic nitro-amines and diamines were then employed (D. R. P. 82748), and in 1897 the nitro derivatives of hydroxydiphenylamine were made use of in the production of **Immedial black**. Improvements in the manufacture of sulphide blues speedily followed, culminating in the discovery in 1900 of **Immedial pure blue** and its homologues from dialkyl-*p*-amino-*p*-hydroxydiphenylamines (D. R. P. 134947).

The addition of copper salts, or even finely-divided copper to the alkali sulphide fusions of diamino- and dialkylamino-hydroxydiphenyl-

amines led in 1901 to the production of green sulphide dyes (D. R. PP. 135410, 148024).

Yellow, orange, and brown sulphide dyes resulted in 1902 from the thionation of tolylene-2:4-diamine and its acyl derivatives with sulphur alone, the products being rendered soluble by subsequent treatment with aqueous sodium sulphide (D. R. PP. 139430, 144762, 152595). These dyes resemble the thiazole colouring matters in the fact that they are formed from aromatic compounds containing methyl and other non-aromatic substituents. The side chains play an essential part in the production of the colouring matter, just as they do in the case of dehydrothiotoluidine and primuline, for diamines, such as *m*-phenylenediamine, without side chains do not furnish these yellow and orange dyes.

Although the problem of producing scarlet and bright-red sulphide dyes has not hitherto been solved, it has been shown that colouring matters of distinctly reddish shade can be obtained by thionating certain of the red dyestuffs, such as the azines, rosindulines, and safranines, in some cases in the presence of copper salts (D. R. PP. 126175, 152373, 161462, 177709, 181125).

These red sulphide dyes, however, are less fast to light than the brown and black dyes of this series, and the yellow sulphide colours also suffer to some extent from this drawback. On this account the greatest development of the sulphide dye industry has taken place in the production of brown, blue, and particularly black dyes, the last of which are now manufactured on an enormous scale owing to their cheapness, fastness, and ease of application.

The discovery of hydron blue and its homologues in 1908 (C. D. R. PP. 218371, 221215, 222640, and 238857) ushered in a new epoch in the history of sulphide dyes, inasmuch as this colouring matter, which is applied as a vat dye, is a serious rival to indigo on account of its fine shade and its fastness to light, and to scouring and bleaching agents. This important development is, moreover, noteworthy from the circumstance that the starting-point in this manufacture is carbazole, a coal-tar product which has not hitherto been utilisable to any adequate extent in the synthetic colour industry.

As the exact chemical constitution of the various commercial sulphide dyes is not in general known with certainty, it will be convenient to group these substances together in accordance with their tinctorial properties.

The firms engaged in the manufacture of sulphide dyes designate their respective products by generic names which are set forth in the following table; the abbreviations in brackets are used throughout this article to indicate the makers or patentees of the various products described.

<i>Manufacturers.</i>	<i>Sulphide dyes.</i>
Aktiengesellschaft für Anilin Fabrikation, Berlin (<i>A.</i>)	Sulphur colours.
Badische Anilin-Soda-Fabrik, Ludwigshafen a/Rhein (<i>B.</i>)	Kryogen "
Gesellschaft für Chemische Industrie in Basel (<i>Bl.</i>)	Pyrogen "
Farbenfabriken vorm. Fr. Bayer & Co., Elberfeld (<i>By.</i>)	Katigen "
Leopold Cassella & Co., Frankfurt a/Main (<i>C.</i>)	Immedial "

<i>Manufacturers.</i>	<i>Sulphide dyes.</i>
Carl Jäger, Düsseldorf-Derendorf (<i>C. J.</i>)	Thiophor Indigo, &c.
Clayton Aniline Co., Ltd., Clayton, Manchester (<i>Cl. Co.</i>)	Clayton black, &c.
Dahl & Co., Barmen (<i>D.</i>)	Cotton blacks, browns, &c.
Anilinfarben und Extrakt-fabriken vorm J. R. Geigy (<i>G.</i>)	Eclipse colours.
Read Holliday & Sons, Ltd., Huddersfield (<i>H.</i>)	Cross dye colours.
L. B. Holliday & Co., Huddersfield (<i>L. B. H.</i>)	Thionone colours.
Kalle & Co., Biebrich a/Rhein (<i>K.</i>)	Thion colours.
Farbwerk Mülheim vorm. A. Leonhart & Co., Mülheim bei Frankfurt (<i>L.</i>)	Pyrol black, &c.
Levinstein, Ltd., Blackley, Manchester (<i>Lev.</i>)	Thionol colours.
The British Dyestuff Corporation (<i>B. D. C.</i>)	
Farbwerke vorm. Meister, Lucius & Brüning, Höchst a/Main (<i>M.</i>)	Thiogene colours, melanogen blue, &c.
Chemische Fabrik Griesheim-Elektron, Werk Oehler (vorm. K. Oehler, Griesheim) (<i>O.</i>)	Thioxine colours.
Société Anonyme des Matières Colorantes et Produits Chimiques de St. Denis, Paris (<i>P.</i>)	Vidal black, thio-catechine.
Chemische Fabriken vorm. Weiler ter Meer, Uerdingen a/Rhein (<i>T.M.</i>)	Auronal black, &c.
Sandoz & Co. (vorm. Kern & Sandoz), Basle (<i>K. S.</i>)	Thional colours.

BLACK SULPHIDE DYES.

Vidal black (*P. Eng. Pats. 23578, 1893 ; 9943, 1894 ; D. R. PP. 85330, 90369*) is produced by heating with alkali polysulphides either *p*-aminophenol or substances capable of yielding this compound. *p*-Nitrophenol (100 parts) is slowly added to 400 parts of crystallised sodium sulphide, $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$, melted in its water of crystallisation; the temperature is raised to 130° , and, when reduction is complete, 75 parts of sulphur are introduced and the mixture heated to 150° – 175° . A vigorous reaction takes place, hydrogen sulphide being evolved freely; finally the mixture becomes too solid to be stirred, and is dried at 180° until quite hard and crisp. The dried mass can then be used directly in dyeing, or the dye may be purified by precipitation from aqueous sodium sulphide with dilute hydrochloric acid. Its solution in alkali sulphide is green, and cotton is dyed in green shades which change to black when the fabric is subsequently chromed, the black shades thus produced are extremely fast to light and scouring agents.

Vidal black is a black mass with bronzy reflex, and its green leuco derivative, produced by aqueous sodium sulphide, can be further changed by powerful reducing agents (zinc and sodium hydroxide) to a reduction product having no affinity for cotton.

The purified dye is obtained by dissolving the crude fusion product in water and precipitating with dilute acetic or hydrochloric acid. The precipitate when washed free from inorganic salts is dried at 110° , extracted with carbon disulphide till free from uncombined sulphur, washed with dry ether and light petroleum, and dried at 90° – 100° . The product is thus obtained in small amorphous black nodules with dark bronzy lustre; it contains about 32 p.c. of combined sulphur.

The inventor has modified the original black by heating *p*-aminophenol and sulphur with resorcinol or *m*-phenylenediamine (*Eng. Pat. 105162, 1917*). A direct black, fast to chlorine,

which does not bronze and is without grey reflection is obtained by adding commercial cresol or phenol to the sulphur black mixture of 2:4-dinitrophenol and aqueous polysulphide (Vidal, Eng. Pat. 141759, 1917).

Vidal black S (D. R. P. 88392) is the soluble sulphite compound of the preceding dye produced by adding 100 kilos. of 15 p.c. Vidal black paste to an aqueous solution containing 50 kilos. of sodium sulphite or bisulphite.

A modified Vidal black is obtained by heating with sulphur at 240° *p*-aminophenol and its homologues with acetanilide, the acetotoluidides, &c. (G. D. R. P. 128361).

Clayton black D (Cl. Co. D. R. P. 106030; Eng. Pat. 21832, 1898). Nitrosophenol (95 parts) is dissolved in 92 parts of sodium hydroxide (38° Bé.), diluted with 500 parts of water and mixed successively with 500 parts of sodium thiosulphate in 300 parts of water and 750 parts of 30–40 p.c. sulphuric acid below 22°. The filtered solution mixed with an alkaline solution of 57 parts of nitrosophenol is heated for 4–6 hours until sulphur dioxide is all evolved, and then cooled, when the precipitated dyestuff is collected.

Clayton black D is soluble in aqueous sodium hydroxide or carbonate to a coal-black solution turned violet by sodium sulphite; it dissolves in concentrated sulphuric acid to a blue solution and when dyed on cotton in sodium sulphide bath, 10 p.c. of colour gives an intense pure black, which is deepened by chromic acid or copper sulphate, and is fast to acids, alkalis, and soap.

Dinitrophenol black; immedial black N; sulphur black T extra; thiophenol black T extra; thionol black; cross dye black B X (D. R. PP. 127835, 136016, 218517; Eng. Pats. 19831, 1896; 13035, 17805, 1903; Fr. Pats. 259509, 267343, 333096). Thirty parts of 2:4-dinitrophenol are slowly added to a solution of 125 parts of sodium sulphide $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$, and 45 parts of sulphur in 150 parts of water, and the mixture boiled under a reflux apparatus (103°–106°) for 25–40 hours. The boiling mass, which assumes a green colour changing to bluish-black, is then poured into water, and the filtered solution is either acidified or oxidised by a current of air. The bluish-black colouring matter is collected and washed free from inorganic salts. The dye is further purified by dissolving in aqueous sodium sulphide, reprecipitating by filtered air and washing the precipitate until free from sodium salts. The product is then dried at 100°–110°, and extracted with boiling carbon disulphide until free from uncombined sulphur. Dinitrophenol black is thus obtained as a bluish-black bronzy mass devoid of crystalline structure. It dissolves in aqueous alkali sulphides to a dark greenish-blue solution, and is practically insoluble in cold concentrated sulphuric acid.

A specimen of cross dye black BX (H.), purified in the foregoing manner, contained 29.0 p.c. of sulphur and 12.5 p.c. of nitrogen. Thionol black O extra (B. D. C.) when similarly isolated, contained 28.0 p.c. of sulphur and 10.4 p.c. of nitrogen. Thionol black OO extra (B. D. C.) contained 36.0 p.c. of sulphur. The black produced by the boiling process in aqueous solutions has been examined by Vetter

(Dissertation, Dresden, 1910), who ascribes the following empirical formulæ $\text{C}_{24}\text{H}_{16}\text{O}_8\text{N}_6\text{S}_7$, or $\text{C}_{24}\text{H}_{16}\text{O}_8\text{N}_6\text{S}_8$, according to the experimental conditions.

The great commercial importance of this colouring matter lies in the fact that it dyes unmordanted cotton in intense black shades which are fully developed by aerial oxidation without subsequent treatment with chromic acid or any other oxidising agent. Moreover, the colour is not affected in tint by after-chroming, and it is remarkably fast to light, acids, alkalis, and scouring and milling agents.

Immedial black NN. The above-described method for making dinitrophenol black is a boiling process carried out at comparatively low temperatures (103°–106°) in aqueous solution, and in this respect the result is an exception to the general tendency, noticed by Croissant and Bretonnière (*v. supra*), for darker shades to be produced at higher temperatures. Vidal, who first suggested the use of dinitrophenol for making sulphur blacks, devised a melting process which leads to products totally different from the black obtained by the boiling process and dyeing cotton in worthless dark-brown shades (Eng. Pat. 16449, 1896; D. R. P. 98437). When, however, the reagents are mixed in the following proportions, dinitrophenol (25 parts), sodium sulphide (125 parts), and sulphur (50 parts), and heated gradually to 160° and maintained at this temperature until the fused product becomes solid (2–3 hours), then a black is obtained, but a departure from these proportions, which correspond with Na_2S_5 , leads to brown products (C. Eng. Pat. 19831, 1896). The product of fusion is dissolved in water and the dye precipitated by acid or air and made into a paste or dried.

Thion black (K.) is a similar product obtained by a melting process at 140°–160° for 2–3 hours, using 35 parts of sodium tetrasulphide and 20.6 parts of sodium dinitrophenoxide (Eng. Pat. 26379, 1903).

Thional black (K. S. Eng. Pat. 26465, 1901) is produced in aqueous solution under pressure at 160°–165° from dinitrophenol (92 parts), sodium thiosulphate (400 parts), 33 p.c. sodium hydroxide (61 parts), and water (800 parts).

Thiophenol black T extra (Bl. Eng. Pat. 13035, 1903) is obtained from dinitrophenol and polysulphide either at 115°–140° under the ordinary pressure, or at 110°–115° under a pressure of 2½ atmospheres, and a greener shade of black is produced either by adding copper salts or 5 p.c. of chloro-2:4-dinitrobenzene (*cf.* D. R. P. 208377; Eng. Pat. 27213, 1906).

The dinitrophenol employed in these operations is prepared by the action of boiling aqueous sodium hydroxide on chloro-2:4-dinitrobenzene, and the latter substance has itself been employed in the boiling process with sodium hydroxide and polysulphide when hydrolysis and thionation occur in one operation (Eng. Pat. 26345, 1904).

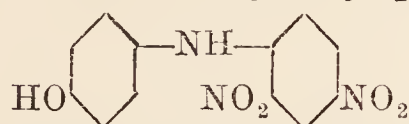
Cross dye black R X (I. B. H.) is produced from a mixture of 2:4-dinitrophenol and picric or picramic acid in the boiling process; it gives a redder shade of black than cross dye black B X, and dissolves slightly in cold concentrated sulphuric acid to a purple-blue solution. Picramic

acid (14 parts), sodium sulphide (60 parts), and sulphur (25 parts) in 50 parts of water give after 24 hours' boiling under a reflux condenser a violet-black dye (*A. Eng. Pat. 7332, 1900*; *D. R. P. 116791*). The dinitrated products of the cresols and chlorophenols also yield various shades of sulphide blacks by the boiling process (*A. Eng. Pats. 7076, 1900*; *15625, 1909*; *D. R. P. 129564*).

Other brands of **Cross dye blacks and blues** (*L. B. H.*) are produced by the polysulphide fusion of sulphonie-, nitro-, amino- or hydroxy-derivatives of benzene, naphthalene, or their homologues (*Eng. Pats. 11370, 1896*; *17740, 1898*).

A sulphide black is claimed to result from the heating of β -naphthol at 160° – 180° , either alone or with 2:4-dinitrophenol (*U.S. Pat. 1274351*).

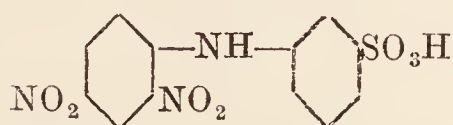
Immedial black V extra (C.). *p*-Aminophenol and chloro-2:4-dinitrobenzene, when boiled in alcoholic solution in the presence of sodium acetate, yield 2:4-dinitro-4'-hydroxydiphenylamine



Fifteen parts of this substance are heated for 5 hours in a reflux apparatus with sodium sulphide crystals (75 parts), sulphur (30 parts), and a small amount of water to 140° – 160° , the dye being precipitated from an aqueous solution of the fused product by acid, carbon dioxide, or air. Cotton is dyed in bluish-black shades, and when oxidised on the fibre with hydrogen peroxide the colour changes to blue (**Immedial blue**, *C. D. R. P. 103861*; *Eng. Pat. 25234, 1907*; *Fr. Pat. 271909*). The immedial black fusion may be carried out under pressure; the 2:4-dinitro-4'-hydroxydiphenylamine (10 parts) and dry sodium tetrasulphide (18 parts) are heated in an autoclave with 50–60 parts of alcohol, and the product, suspended in water, is converted into immedial blue by the addition of hydrogen peroxide (*C. D. R. PP. 132424, 137784*; *Eng. Pat. 5385, 1900*). The colour on cotton is fast to chlorine, light, and scouring agents.

When immedial black, eclipse black, or kryogen black is heated up to 200° with 1:8-dinitronaphthalene and sodium polysulphide, a black is produced which is more stable to oxidising agents than that from either of its generators (*v. Fast black, B. Fr. Pat. 319790*).

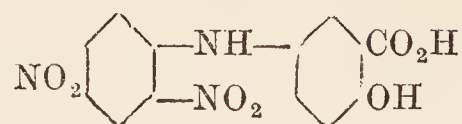
Cotton black (*D. Eng. Pat. 13167, 1898*; *D. R. PP. 101862, 105058*). Chloro-2:4-dinitrobenzene is condensed with 3-aminobenzenesulphonic acid and the resulting 2:4-dinitrodiphenylamine-3'-sulphonic acid



(12 parts) is thionated with sodium sulphide (60 parts), sulphur (8 parts), and water (5 parts), the temperature being raised to 200° – 220° . The colouring matter dyes in greenish-black shades which are not affected by oxidising agents. 2:4-Dinitrodiphenylamine-4'-sulphonic acid gives a coal-black sulphide dye absolutely fast to milling.

Sulphanil black C (K.). Chloro-2:4-dinitrobenzene is condensed with 4-aminosalicylic acid,

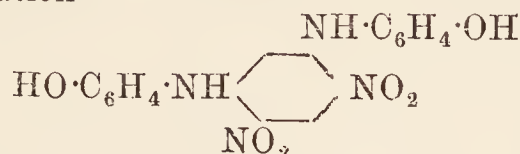
the product, 2:4-dinitro-4'-hydroxydiphenylamine-3'-carboxylic acid



is thionated at 150° with an equal weight of sulphur and 2.5 parts of sodium sulphide (*D. R. P. 129885*).

Katigen black (By.) is produced in a similar way by the thionation of 2:4-dinitro-2'-hydroxydiphenylamine-3'-carboxylic acid (*D. R. P. 112182*).

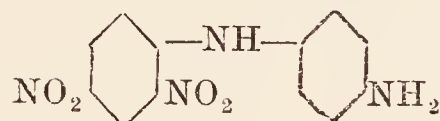
Kryogen blacks G, BG, B, N, result from the condensation



of dinitro-*m*-dichlorobenzene with *p*-aminophenol (2 mols.), and its sulphonie and carboxylic acids, these three reagents on thionation giving respectively deep black, greenish-black, and bluish-black shades (*B. Eng. Pat. 20232, 1899*; *D. R. P. 112298*).

Indocarbon black S, SF (C.). The indophenol obtained by condensing carbazole (40 parts), nitrosophenol (30 parts) in 1100 parts of concentrated sulphuric acid at 15° , is heated with sodium sulphide, sulphur, aqueous sodium hydroxide, and copper sulphate in a reflux apparatus at 125° for 18 hours. The product, which is precipitated by air from sodium sulphide solution, gives full bluish-black shades very fast to chlorine (*D. R. P. 221215*). Similar dyes are produced from halogenated carbazoles and the homologues and substitution products of nitrosophenols (*v. D. R. PP. 222640, 224590, 224591, 227323, 235364, 235836, 238857*).

Auronal black (T. M.) is prepared from 2:4-dinitro-4'-aminodiphenylamine (36 parts)



derived from chloro-2:4-dinitrobenzene and *p*-phenylenediamine by heating with sodium sulphide (180), sulphur (60), water (60), and glycerol (15 parts), the last substance serving to regulate the temperature of the boiling solution. At 165° a colour is produced, dyeing in dark-blue shades rendered faster by after-chroming. This product gives reddish-blue and violet solutions in concentrated sulphuric acid and aqueous sodium hydroxide respectively. At 170° – 180° the fused product gives a bluish- or greenish-black colour, the colours in concentrated sulphuric acid being greenish-blue and black respectively. At 180° a spontaneous generation of heat occurs and an olive sulphide dye is produced (*D. R. P. 144119*; *Eng. Pat. 11733, 1901*).

The above diphenylamine derivative is converted into a greenish-black compound by heating up to 150° with sodium polysulphide and hydroxide (*K. D. R. P. 134704*); in the absence of caustic alkali an insoluble product is obtained.

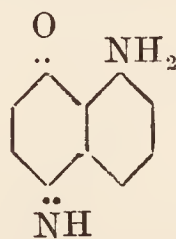
Pyrol black (L.). *p*-Aminophenol (11 kilos.) is heated with its hydrochloride (15 kilos.) for 10 hours at 170° , or for 5–6 hours at 180° – 220° ; 12 kilos. of the condensation product insoluble

in dilute acids are heated at 180°–220° with 30 kilos. of sodium sulphide and 4 kilos. of sulphur. The fused product dissolves in water to a dark blue solution from which acids precipitate the black dye. The leuco compound with zinc-dust and alkali is red; the dyed black is fast to light and scouring agents.

Autogene black (P.) dyeing cotton direct from a Glauber's salt bath in bluish-black shades is produced by the action of sulphur chloride on phenol or its homologues, or on aromatic amines, the product being then treated with *p*-amino- or diamino-hydroxydiphenylamine, followed by sodium sulphide fusion at 150°–200° (Eng. Pats. 18409, 1899; 999, 1901; D. R. PP. 113893, 131468).

Melanogen blue B, BG, D. When 1:5-dinitronaphthalene, dissolved in warm concentrated sulphuric acid, is treated with hydrogen sulphide or a metallic sulphide, a compound is produced which is precipitated as its insoluble zinc chloride compound from the diluted solution. This substance (1 kilo.), which is an intermediate product in the preparation of naphthazarin, is heated with sodium sulphide (5 kilos.) and sulphur (1 kilo.) at 150°–180° for several hours, when the fused product is poured into water and the filtered solution evaporated to dryness. This soluble colouring matter dyes cotton in fast greyish-blue shades which are not altered during dyeing by aerial oxidation, but subsequent treatment with copper sulphate develops a fast bluish-black shade. Subsequent treatment with chromium, nickel, or cobalt salts give bluish-blacks, whilst zinc, cadmium, or aluminium salts develop bright blue shades (*M. D. R. PP.* 114266, 114267, 116417, 119248, 120899, 124507). The non-sensitiveness of these dyes to aerial oxidation distinguishes them from the typical sulphide dyes which furnish oxidisable leuco derivatives.

Kryogen blue B, G, R, are similar dyestuffs produced by heating the reduction products of 1:5- and 1:8-dinitronaphthalene (*B. D. R. PP.* 88236, 92471, 92472) with sodium sulphide and sulphur; violet and blue shades are produced at 100°, whilst blacks are obtained at 150°–200° (*B. D. R. PP.* 103987; *M. ibid.* 128118). The intermediate naphthazarin product



is converted into a wool dye by alkali thiosulphate and then by the action of sulphites or bisulphites into soluble compounds, which dye chrome mordanted cotton in greenish-black shades (*B. D. R. P.* 147945).

Fast black B and BS. The former of these colouring matters consists of a mixture of two dyes produced by boiling 1:8-dinitronaphthalene with 3–5 molecules of aqueous sodium sulphide (1:120), then acidifying and boiling for 2 hours longer.

Fast black BS is produced by heating at 93° for 1 hour 200 parts of **fast black B** (30 p.c. paste) with 98 parts of sodium hydroxide (30°Bé.) or the equivalent amount of sodium

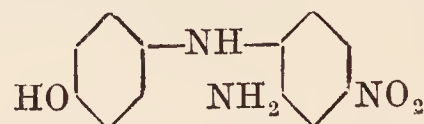
sulphide. The soluble product gives intense black shades on cotton (*B. D. R. PP.* 84989, 88847; Eng. Pats. 10996, 1893; 22603, 1894).

Anthraquinone black. 1:4'-Dinitro-anthraquinone (50 parts), sodium sulphide (250 parts), and sulphur (75 parts) are heated together until the product is soluble in water to a bluish-green solution.

Cotton is dyed with aqueous sodium sulphide in intense black shades. The colour is slightly soluble in alcohol forming a green solution; with concentrated sulphuric acid the colour is greyish-black (*B. D. R. PP.* 91508, 95484; Eng. Pat. 15242, 1895).

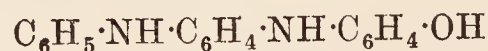
SULPHIDE BLUES.

Pyrogen direct blue (Bl.), the first blue sulphide dye discovered, is prepared from 2:4-dinitro-4'-hydroxydiphenylamine (m.p. 187°–188°) or its reduction product (m.p. 196°–197°)



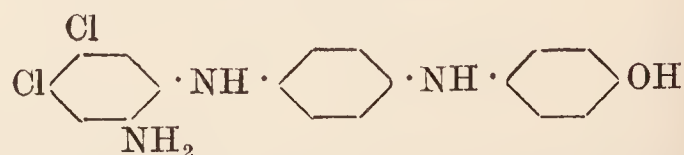
Ten parts of either of these substances are heated with 18 parts of anhydrous sodium tetrasulphide and 60 parts of alcohol in an iron or enamelled autoclave at 135°–145°. The reaction proceeds smoothly in alcoholic solution, colour formation begins at 110°, and after 3–4 hours the pressure reaches 8–10 atmospheres. Cotton is dyed in dark violet-blue shades with 2 p.c., and in black bluish-violet shades with 5 p.c. of the dye (Eng. Pat. 5385, 1900; D. R. P. 132424). The violet tint of the dye is increased by suspending it in water and adding hydrogen peroxide; ozonised air or steam produces a similar effect which is probably due to elimination of NH₂ groups. The violet product is fast to chlorine, light and scouring agents (D. R. P. 137784). When the temperature of the autoclave in the foregoing process is raised to 160°–170° **pyrogen grey** is produced, the shade of which is not affected by oxidising agents.

Pyrogen indigo (Bl.). Phenyl-4-amino-4'-hydroxydiphenylamine



27.6 kilos., is heated with dry sodium pentasulphide (55 parts) in 150 litres of alcohol under reflux for 24 hours. The solvent is distilled off, the residue dissolved in water, and the dye precipitated by air as a dark blue powder, dissolving in aqueous sodium sulphide to a blue solution and dyeing cotton in indigo blue shades (D. R. P. 150553).

The dichlorinated compound



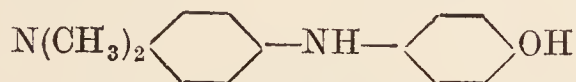
is also converted into a blue sulphide dye by heating with alkali polysulphide (Eng. Pat. 118103, 1918), whereas thionation of the azo derivative from picramic acid and a cresol gives blue-black colours (Eng. Pat. 127143, 1918).

Immedial pure blue (Immedial sky blue) (C.). Nitrosodimethylaniline is reduced with iron powder in dilute acetic acid solution. After

removing the iron the filtrate is mixed with the calculated amount of phenol in aqueous solution, and the mixture oxidised with air in the presence of copper salts. The resulting indophenol



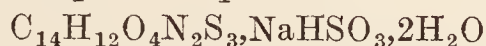
is then reduced to 4-dimethylamino-4'-hydroxydiphenylamine



(m.p. 161°–162°) a base which is also obtained by heating *as*-dimethyl-*p*-phenylenediamine with *p*-aminophenol hydrochloride at 150°.

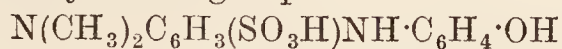
Twenty-five kilos. of this base are added gradually to 50 kilos. of crystallised sodium sulphide, 12.5 kilos. of sulphur, and 10 litres of water heated to 90°. The mixture is then heated under a reflux apparatus at 110°–115°, a green pitch separates and gradually redissolves. After 24 hours the product is dissolved in 500 litres of water, and the colour precipitated with 50 kilos. of salt. Cotton is dyed in shades resembling methylene blue which are superior to indigo blue in brilliancy of tint and in fastness to light, chlorine, acids, and milling (Eng. Pat. 16247, 1900; D. R. P. 134947, 141752; Fr. Pats. 303524, 308669).

The Bisulphite compound



is the first crystallisable derivative obtained from sulphide dyes, and is used in purifying the foregoing colouring matter. The melt is dissolved in 700 litres of water and treated with sodium hydrogen sulphite until the additive compound is precipitated. The solution is then heated to 90°, when this substance dissolves, leaving the impurities. The bisulphite compound separates on cooling in yellowish needles, and is washed with brine solution; it dyes wool in acid baths, and with the aid of oxidising agents (chromates, copper salts, &c.) gives indigo blue shades. The colouring matter is regenerated by digesting the additive compound with dilute sodium hydroxide solution. The lower homologues of immedial pure blue have been described (D. R. P. Anm. K. 13405, 1900; D. R. P. 133481).

Eclipse blue (G.). The indophenol from dimethyl-*p*-phenylenediamine and phenol when treated with alkali sulphites gives a sulphonic acid with its sulphur in the nucleus containing the tertiary amino groups

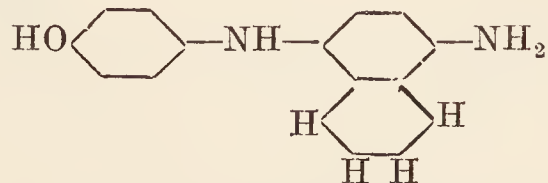


The sodium salt of this acid heated at 120°–140° with an equal weight of sulphur and 2½ parts of crystallised sodium sulphide, gives a blue solution from which the colouring matter is precipitated by air, hydrogen peroxide, or alkali hypochlorite; cotton is dyed in very fast pure blue shades (Eng. Pat. 12578, 1901; D. R. P. 129325).

Immedial indone (C. D. R. P. 199963; Eng. Pat. 58, 1902; Fr. Pat. 317219; U.S. Pat. 709151). The indophenol from *p*-aminophenol and *o*-toluidine is heated with sodium polysulphide in alcoholic or aqueous solution (120°). The blue dye has a remarkable affinity for the cotton fibre, being much superior in this respect to its lower homologue from phenol and aniline. A brighter blue of redder shade has been obtained

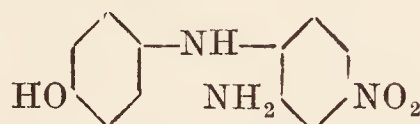
by heating the foregoing indophenol with sulphur alone at 190°–200° for 2 hours in the presence of hydrated chromic oxide. The product is directly applicable in sulphide solution as a cotton dye (K. S. Eng. Pat. 12879, 1903).

A sulphide colour dyeing cotton in fast pure blue shades is produced by thionating the indophenol



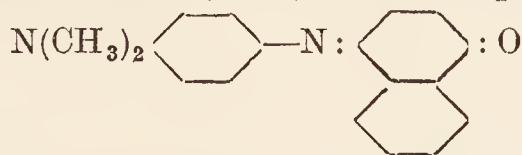
derived from *ar*-tetrahydro-*α*-naphthylamine, a base which has not hitherto been regarded as an industrial possibility (U.S. Pat. 1175230; D. R. P. 338817).

Thion blue B (K.). 2 : 4-Dinitro-4'-hydroxydiphenylamine, the condensation product of chloro-2 : 4-dinitrobenzene and *p*-aminophenol, is partially reduced to 4-nitro-2-amino-4'-hydroxydiphenylamine

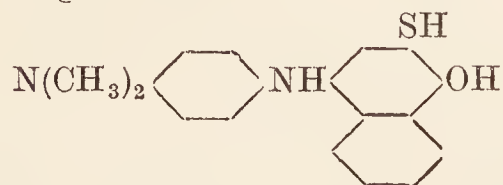


and this base heated with carbon disulphide, whereby the thiocarbamide derivative is produced. Five parts of this compound are heated for 10 hours at 145° with sodium sulphide (40 parts) and sulphur (24 parts). The fusion product is dissolved in water and the dye precipitated by the continued passage of air in the presence of sodium chloride. The shade on cotton is bluish-green, changed to pure blue by hydrogen peroxide, subsequent treatment with stannic chloride increasing the fastness of the dye (Eng. Pat. 19332, 1901; D. R. P. 139099).

Thiophor indigo (C. J.). The indophenol



(25 parts) produced from *α*-naphthol and *p*-aminodimethylaniline is heated in a reflux apparatus at 115° with 40 parts of crystallised sodium sulphide and 15 parts of sulphur. The leuco-indophenol which separates as an oil slowly reacts with the thionating mixture during 8–10 hours with evolution of hydrogen sulphide. The colouring matter, which crystallises from benzene in small prisms with a coppery lustre, still possesses the indophenol character of being hydrolysed by acids. On this account the leuco derivative of the dye is represented by the following formula :—



The solution of the dye in aqueous sodium sulphide is pale greenish-yellow, and, unlike the great majority of sulphide colouring matters, this product is soluble in the organic media, including ether.

Various shades of blue and violet are produced by changing the base employed in producing the indophenol; *p*-phenylenediamine and 2 : 4-tolylenediamine give rise to dark violet

tints. The temperature is generally kept below 160°, and alterations in tinctorial properties are effected by introducing alcohol or glycerol into the thionating mixture. The dyed colours are fast to light, alkalis and scouring agents, but are destroyed by acids (D. R. P. 179839; Eng. Pat. 17540, 1905; Fr. Pat. 357587; U.S. Pat. 821378).

Blue sulphide colours for wool dyeing from an acid bath are obtained by fusing α -naphthylamine-4 : 8-disulphonic acid or α -naphthylamine-4 : 6 : 8-trisulphonic acid with sulphur and an alkali, the colouring matter being precipitated by aerial oxidation from hot neutral or alkaline solutions (K. Fr. Pat. 471230).

A series of sulphide blues having the property of dyeing weak blue shades from sodium sulphide baths, and remarkably fast blue shades when employed as vat dyes, are produced by heating with sodium polysulphide (Na_2S_5 — Na_2S_8) in alcoholic solution, the indophenols from dialkyl-*p*-phenylenediamines and phenol and its ortho- and diortho-chloro derivatives (B. D. R. PP. Anmeldung, 60985 and 62302, 1911). Similar sulphide blues capable of employment as vat dyes are obtained in a similar manner from the indophenolthiosulphonic acids (prepared from alkyl-*p*-diaminethiosulphonic acids and phenol), or from the corresponding thiazines (B. D. R. PP. 153361; Anmeldung, B. 60984, 1911).

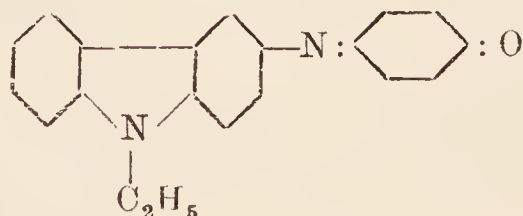
Other commercial brands of sulphide blues :—**Immedial direct blue, B, JB, R, OD**; **Immedial indogene B, GCl**; **Thiogene blue, B, R, 2R**; **Thiogene cyanine B, O, G**; **Thiogene deep blue RL, 2RL**; **Thiogene new blue JL, Bl, 2RL**; **Thionol blue 2B, RB, 2RF**.

HYDRON BLUE SERIES.

Hydron blue. The indophenol



from carbazole and nitrosophenol, prepared by dissolving carbazole in 10 parts of concentrated sulphuric acid and adding *p*-nitrosophenol (1 mol.) dissolved in 10 parts of the same solvents at 30°, is isolated by pouring the acid solution on to ice. This intermediate is heated in alcoholic solution with excess of sodium polysulphide Na_2S_6 until the product is only sparingly soluble in dilute aqueous sodium sulphide. The alcohol is then distilled off and the residue is freed from incompletely thionated substances by repeated digestion with aqueous sodium sulphide. The insoluble product, a bluish-black powder with metallic reflex, dissolves in alkaline hydrosulphite solution to a clear yellow vat which is employed in dyeing full blue shades on cotton. These dyeings surpass indigo in their fastness to light and scouring agents. The shade of colour thus produced, **Hydron Blue R**, is modified by substituting for the foregoing intermediate the indophenols produced by condensing *p*-nitrosophenol with the N-alkyl and N-aryl derivatives of carbazole



The indophenol of N-ethylcarbazole when refluxed for 48 hours with alcoholic sodium sulphide containing flowers of sulphur yields a crude colouring matter, which when purified from sulphide colour and excess of sulphur by extraction with warm aqueous sodium sulphide yields a vat dye known in the trade as **Hydron Blue G** (C. D. R. PP. 218371, 221215, 222640, 224590, 224591, 224951, 227323, 235364, 238857, 247443; Eng. Pat. 18822, 1909). The thionation of the indophenols is accelerated and the resistance of the vat dyes to bleach liquors is increased by employing halogenated nitrosophenols or carbazoles in the production of the intermediate. The indophenols from carbazole and N-ethylcarbazole when condensed with 2 : 4-dinitrochlorobenzene yield a condensation product (m.p. 185°–186°) which on treatment with alcoholic alkali polysulphide furnishes a blue vat dye (C. D. R. P. 247688).

Carbazole condensed with arylsulphimino-arylene chloroimides



in concentrated sulphuric acid give carbazole indamines. The product obtained by thionating these indamines or their leuco derivatives either with or without copper compounds is a mixture of a true sulphide dye soluble in warm aqueous sodium sulphide, giving intense blue shades on cotton and of a vat dye of the hydron blue class insoluble in aqueous alkali sulphide, but furnishing blue shades of great fastness from a hydrosulphite vat (Eng. Pat. 15949, 1914). Carbazole-indophenolsulphonic acids on prolonged thionation furnish dyes giving deep blue fast shades on cotton (C. Fr. Pat. 462316).

Hydron Blue R is printed on textile fabrics with alkaline benzylsulphanilate made up into a paste with starch and grape sugar solution (D. R. P. 252267).

SULPHIDE GREENS.

Thiochem sulphur green, Sulphur olive green, produced by the polysulphide fusion of benzene-azophenol and a copper salt at 180°–200°, dye in dark green shades fast to milling, cross dyeing and light. When the melt is heated to 250° **Sulphur Brown R** is produced.

Thionone brilliant green GG conc. (L. B. H.). Phenyl- (or *p*-tolyl) α -naphthylamine-8-sulphonic acid and *p*-aminophenol are oxidised together with sodium hypochlorite at temperatures below 5°. The oxidation product is reduced with cold sodium sulphide to 1-phenyl (or *p*-tolyl)-amino-4'-hydroxyphenyl-4-aminonaphthalene-8-sulphonic acid. This substance is boiled with aqueous sodium polysulphide and copper powder (or copper sulphate) at 120° for 20 hours; the product is dissolved in water and the dye salted out. This sulphide green is particularly fast to light and washing.

Italian green, Verde Italiano (Lepetit, Dollfus, and Gansser, D. R. P. 101577). *p*-Nitrophenol (12.5 kilos.), copper sulphate (4.5 kilos.) in 30 litres of water, are mixed with sodium hydroxide (19 kilos.), sulphur (17.5 kilos.), in 17 litres of hot water, and the mixture gradually heated to 210°, ammonia being evolved. Cotton is dyed in dull grass-green shades which appear pure green by artificial

light. Hydrogen peroxide, chromic acid, or copper sulphate change the colour to blue-black, and concentrated oxidising agents discharge the colour, this reaction being made use of in printing with the dye.

Pyrogen green B, FB, FF, 2G, 3G (*Bl. D. R. P.* 148024), **pyrogen dark green B.** *p*-Aminophenol (8 parts), sodium sulphide (50 parts), sulphur (20 parts), copper bronze (1 part), and water (100 parts) are heated to 170° in 3 hours. Cotton is dyed in olive-green shades; copper is present in the ash of the dyed fibre.

The greater the amount of copper bronze the more olive is the shade of colour produced. Other variations in the tint are brought about by using the homologues and substitution products of *p*-aminophenol.

Pyrogen olive N (*G. D. R. P.* 135335). *p*-Hydroxybenzylidene-*p*-nitroaniline, *p*-nitrobenzylidene-*p*-aminophenol and similar methylene and benzylidene derivatives of *m*- and *p*-diamines, and aminophenols are heated to 180°–200° with sodium polysulphide with or without metallic salts.

Eclipse green G (*G. D. R. P.* 135410; *Eng. Pat.* 26448, 1901). The indophenol from *p*-aminodimethylaniline and phenol is treated with sodium sulphite, and the resulting sulphonic acid (40 parts, Na salt) heated with sodium sulphide (100 parts), sulphur (40 parts), and copper sulphate (10 parts) in a reflux apparatus at 125°–130°. The dye is precipitated by air from its solution in aqueous sodium sulphide; it dyes in yellowish-green shades fast to light and soap.

Thion green B (*K. D. R. P.* 138104; *Eng. Pats.* 9619, 16931, 1902; *Fr. Pats.* 320701, 323489). Hydroxyphenylthiocarbamide and hydroxythiocarbanilide are heated respectively with sodium polysulphide at 140°–180°, the former gives a blue-green and the latter a mignonette-green, both dyes are turned bluer by chromic acid, and are insoluble in strong sulphuric acid. The dye is purified by dissolving the fused mass in water, acidifying slightly, filtering off the precipitated sulphur, and salting out the colour in the filtrate.

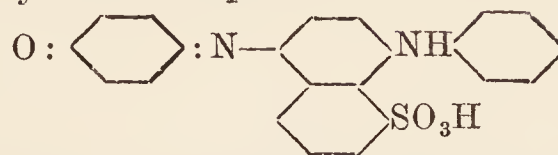
Immedial green. 4-Dimethylamino-4'-hydroxydiphenylamine (50 kilos.) is added to a solution of sulphur (31 kilos.) in crystallised sodium sulphide (124 kilos.). When the base has dissolved, copper sulphate (10 kilos.) is added, and the temperature raised to 120° and maintained for 24 hours. The dye is precipitated by salt or calcium chloride from the resulting solution; it dissolves in strong sulphuric acid to a green solution, and in aqueous sodium sulphide or hydroxide to a reddish-violet solution. The bluish-green shade on cotton is very fast (*C. D. R. P.* 129540).

An olive-green (*O. D. R. P.* 146064) is obtained by heating diformyl-*m*-phenylenediamine with sodium polysulphide at 110°, and then with the further addition of zinc chloride at 230°.

A yellow sulphide dye is formed by heating together of 5-aminocymene, 2:4-tolylene-diamine and sulphur, but a green dye is produced by heating a mixture of acetylaminocymene, sulphur and a *p*-hydroxy aromatic compound (*U.S. Pats.* 1314928, 1314929).

The 1:8- derivatives of naphthalene are employed in producing sulphide greens. Phenyl-

α -naphthylamine-8-sulphonic acid and *p*-aminophenol yield an indophenol



which gives a green on heating with sodium polysulphide in the presence of copper sulphate. The perimidines produced by condensing 1:8-naphthylenediamine with aldehydes, ketones, and aliphatic acids (*Annalen*, 1909, 365, 53; *Ber.* 1909, 42, 3674) yield indophenols with *p*-aminophenol, and its chloro-derivatives (*e.g.* 2:6-dichloro-*p*-aminophenol). These indophenols, when heated for 60 hours in a reflux apparatus with alcoholic sodium polysulphide, give rise to very fast dark green colouring matters (*A. D. R. P. Anmeldung*, 20316, 1911).

Other commercial brands of sulphide greens:—
Immedial deep green G; Thionol green 3G; Thionol brilliant green GX, 3GX, 4GX; Thionol dark green; Thiogene green G, GG, GL; Thiogene olive green GG, GGN.

SULPHIDE BROWNS.

Cachou de laval (P.) is usually prepared from sawdust and other waste products allied to cellulose by heating these materials with sodium polysulphide at 250°–300°, the higher the temperature the darker the shade of brown produced (*cf.* Richardson and Akroyd, *J. Soc. Chem. Ind.* 1896, 328).

In all probability the final products of this reaction are phenolic in character, inasmuch as cellulose yields phenol on distillation, and the latter on oxidation passes into phenoquinone, a substance containing three benzene nuclei, which on heating with alkali polysulphide under pressure gives a dye resembling cachou (Wichelhaus, *Ber.* 1872, 5, 248; 1907, 40, 126; 1910, 43, 2926). A similar brown sulphide dye is produced by heating crude cresol with sodium polysulphide at 170°–250° (*By. D. R. P.* 102897; *Eng. Pat.* 22417, 1895).

The drain on coal-tar products for high explosives during the war led to a resumption of experiments in the production of sulphide dyes from vegetable sources. Gums or gum resins from plants of the genus *Xanthorrhoea*, or the nitro, nitroso, or azo derivatives of yacca gum or of Congo resin were put through the alkali sulphide fusion, yielding various shades of bronze, grey, or black (*Eng. Pats.* 194353, 105118, and 105119).

Cachou de laval S is the soluble product formed by digesting the precipitated colouring matter of cachou with alkali sulphites or bisulphites; it is used in printing (*D. R. P.* 88392).

Thiocatechin (*P. D. R. P.* 82748; *Eng. Pat.* 3431, 1895; *Fr. Pat.* 239714; *U.S. Pat.* 561276; *Ber.* 1880, 13, 1226). The acetyl derivatives of aromatic diamines and nitro-amines are heated either with sulphur alone or with sulphur and sodium sulphide at 200°–250° for 3 hours.

The dye dissolves in aqueous sodium sulphide to a yellowish-brown solution, and when dyed on cotton requires to be fixed by subsequent oxidation. Various shades of yellow and brownish-yellow are produced by heating with 2 parts of sulphur, the following aromatic substances: acetyl-*p*-phenylenediamine, aceto- α -

naphthalide, acetyl-*p*-nitroaniline, diacetyl-di-*o*-nitrobenzidine, and the acetyl derivatives of nitro-*o*- and *p*-toluidine.

$[\text{CH}_3 : \text{NH}_2 : \text{NO}_2 = 1 : 2 : 4 \text{ and } 1 : 4 : 2]$

In the manufacture of 2:4:6-trinitrotoluene (T.N.T.) a small proportion of *m*-nitrotoluene is formed which further nitrated yields 2:3-dinitrotoluene, 3:4-dinitrotoluene, 2:4:5-trinitrotoluene and 2:3:4-trinitrotoluene. These waste products when fused with alkali polysulphide give thionated colouring matters dyeing in khaki brown shades (Eng. Pat. 111738).

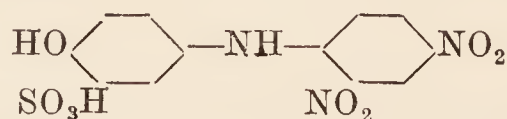
Thiocatechin S is the soluble product obtained by digesting thiocatechin with aqueous sulphites or bisulphites.

Cattu Italiano, sulphine brown (Lepetit, Dollfus, and Gansser, D. R. P. 118701; Eng. Pat. 18900, 1899; Fr. Pat. 290714). Turkey-red oil (5 parts), the higher fatty acids, and especially the unsaturated acids and their esters and alkali salts, when heated with sodium carbonate (12 parts) and sulphur (10 parts) at 320°–330°, evolve carbon dioxide, hydrogen sulphide, and volatile organic matter. The product is a black porous mass readily soluble in water. In spite of the different starting materials which are utilisable in this process, the colouring matter is very constant in properties; it dyes cotton brown from a bath containing sodium chloride in shades which are brighter than the cachous, but less fast to light and chlorine. The dye dissolves in water or aqueous sodium sulphide to solutions which are green to blue in colour, depending on the temperature at which the colouring matter was originally produced.

Thion brown (K. D. R. P. 157540; Eng. Pat. 18489, 1896; Fr. Pat. 315648; U.S. Pat. 723448). Chrysoidine base R (*H.*) (*v.* AZO-COLOURING MATTERS), benzeneazotolylene-2:4-diamine (30 parts) are added to crystallised sodium sulphide (80 parts) and sulphur (30 parts) at 110°–120°, and the temperature raised to 160°, when the azo compound is decomposed with elimination of aniline. The viscid mixture is then baked for 1–2 hours at 160°–170°, and finally for 3–4 hours at 200°–220°, when a brownish-black powdery mass is produced which dyes cotton in intense yellowish-brown shades very fast to light. The dye is precipitated by acids from its alkaline solutions, dissolving as a dark brown mass in alcohol or concentrated sulphuric acid to brown solutions.

Benzeneazo- α -naphthylamine or its derivatives give sulphide browns when heated with sulphur in presence of *m*-tolylenediamine (U.S. Pats. 1251368, 1251369). These reactions indicate that methyl groups are conducive to the formation of dyes of the thion brown type, thus suggesting a thiazole constitution.

Sulphanil brown (K. D. R. P. 125584). 2:4-Dinitro-4'-aminodiphenylamine, prepared from chloro-2:4-dinitrobenzene and *p*-phenylenediamine is converted by means of aqueous alkali sulphite at 150° (46 p.c.) into the sulphonic acid.

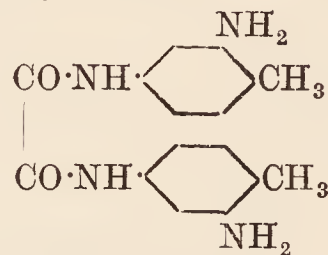


This compound (40 parts), dissolved in

twice its weight of water, is heated at 140°–160° with sodium sulphide (80 parts), sulphur (30 parts), and water (100 parts) until the mass is dry. The aqueous solution of the dye is violet-black changed to brown by caustic alkali.

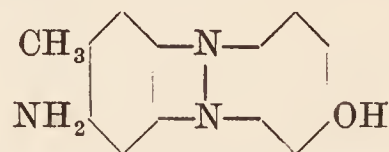
Cotton brown (D. D. R. PP. 102821, 106039). The higher nitrated derivatives of diphenylamine obtained by treating the base with concentrated sulphuric and nitric acids at 25°–60° yield a brown dye when cautiously reduced with sodium sulphide or polysulphide, and the reduction product dried at 200°. The colour is soluble in water, and dyes in cold or hot baths (*cf.* Eng. Pat. 18924, 1903).

Eclipse brown, N, R, B, G, 3G, V (G. D. R. PP. 125586, 125587, 126964, 128659; Eng. Pat. 1644, 1901; Fr. Pat. 306655). Tolylene-2:4-diamine (34 parts), oxalic acid (17 parts), sodium sulphide (120 parts), and sulphur (40 parts) are heated to 225°–250°, and then to 300°. The process may be varied by taking molecular proportions of the diamine and of tolylene-2-amino-4-oxamide



and the polysulphide may be replaced by a solution of sulphur in aqueous sodium hydroxide. The dye dissolves in water to a chestnut-brown solution, being precipitated therefrom by boiling with dilute mineral acid. Hydrogen sulphide is evolved on reducing the compound with zinc-dust. In these condensations the oxalic acid may be replaced by succinic and phthalic acids, the latter giving rise to brown colouring matters dyeing very fast catechu shades.

A brown colouring matter of the immedial series, dyeing cotton in very fast shades closely resembling natural catechu, is produced by oxidising a mixture of *p*-aminophenol and tolylene-2:4-diamine to 2-methyl-3-amino-6-hydroxyphenazine



and by heating the azine obtained from 15.8 parts of *p*-aminophenol with 100 p.c. sodium sulphide (42 parts) and sulphur (80 parts) for 20 hours at 135° (C. D. R. P. 208109; Fr. Pat. 382412; *cf.* By. Eng. Pat. 19548, 1907; B. D. R. P. 147990). Similar fast catechu shades are produced by heating at 250° tolylene-2:4-diamine (2 parts), acetyltolylene-2:4-diamine (1 part), and sulphur (8 parts), the product being ground with 3 parts of sodium hydroxide and warmed at 130° (A. D. R. PP. 221493, 229154; Eng. Pat. 24703, 1909; Fr. Pat. 419665).

A mixture of methylenecrescinol or its polymerides (Ber. 1892, 25, 947; 1894, 27, 2888), *p*-phenylenediamine, sodium sulphide, and sulphur when heated gradually to 200°–220° gives very fast yellowish catechu shades (O. D. R. P. 167429; Eng. Pat. 13950, 1905; Fr. Pat. 355783).

Immedial brown B, dark brown A (*C. D. R. P.* 112484; *Eng. Pat.* 25754, 1899; *Fr. Pat.* 295593). 4-Hydroxy-4'-aminodiphenylamine is boiled with aqueous sodium hydroxide and the product heated to 160° with sodium polysulphide. The two changes may be effected in one operation. This colouring matter gives on cotton intense yellow-brown shades, rendered yellower and faster by after-chroming.

Among other sulphide browns of similar origin to the foregoing colouring matters may be mentioned the following:—

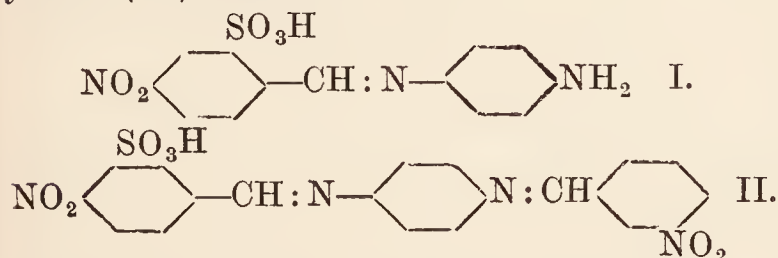
Katigen brown (*By.*); **Sulphur brown G** (*A.*); **Sulphur cutch** (*A.*); **Kryogen brown** (*B.*); produced from 1:8-dinitronaphthalene; **Immedial cutch, immedial khaki, immedial catechu** *O.G.* and *O.R.* (*C.*).

Acenaphthene, a coal-tar product having few industrial outlets, is converted into a reddish-brown sulphide dye by heating with 3-2 parts of sulphur at 250°-300°; the dyeings are remarkably fast to washing and chlorine (*Wylér and Levinstein, Eng. Pat.* 124589, 1918).

The hydrocarbon, cymene, a by-product of the sulphite cellulose process when oxidised and nitrated is converted into mono- and di-*p*-toluic acids, which yield brown sulphide dyes on thionation (*Eng. Pat.* 128099).

SULPHIDE YELLOWS.

Pyrogene yellow M, O, OR, 3R (*Bl. D. R. P.* 135335; *Eng. Pat.* 1007, 1900; *Fr. Pat.* 295712). These colouring matters were the first sulphide yellows discovered, and are produced by heating with sodium sulphide and sulphur (either with or without metallic salts), various condensation products of aromatic *p*-diamines, and amino- and diamino-phenols with formaldehyde, benzaldehyde, the nitrobenzaldehydes, and nitrobenzyl chlorides. The compounds with these aldehydes are of the nature of anhydro bases (*Schiff bases*). The two following derivatives, which may be regarded as typical of the members of the series, give respectively in the polysulphide fusion colours dyeing in greyish-yellow (I.) and orange-yellow (II.) shades.



Other derivatives give rise to different shades; methylene-*p*-aminophenol

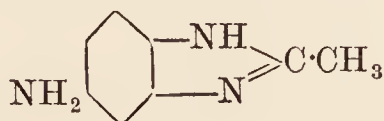


gives a brown, whereas *p*-nitrobenzylidene-*p*-aminophenol

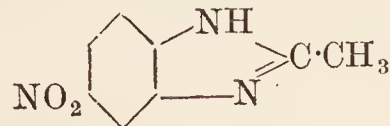


furnishes an olive dye.

Kryogen yellow R (*B. D. R. P.* 142155). 2:4-Dinitroacetanilide when reduced with iron filings and dilute acetic acid yields the anhydro-base, 5-amino-2-methylbenziminazole



This base is heated at 200°-230° for 2-3 hours with 2 parts of sulphur, the product ground with an equal weight of sodium sulphide, dissolved in water, the mixture dried and baked at 200°-230° for 1-2 hours. This colouring matter is diazotisable on the cotton fibre. A similar dye giving greener shades is produced by heating the nitro-anhydro base



with sulphur and an equal weight of benzidine at 200°-240° until hydrogen sulphide is no longer evolved (*T.M. D. R. P.* 157862; *Eng. Pat.* 5449, 1905; *cf. A. D. R. PP.* 121463, 146916, 147403, 147729, 150915, 152717, 154108)

Immedial yellow D (*C. D. R. PP.* 139430, 141576; *Eng. Pat.* 11771, 1902; *Fr. Pat.* 321122). Tolylene-2:4-diamine (50 kilos.) and sulphur (100 kilos.) are heated gradually during 2 hours up to 190°. The amorphous sulphur compound produced is brownish or orange-yellow, insoluble in all ordinary media, dilute acids, or aqueous alkalis, but dissolving slightly in concentrated sulphuric acid to a brown solution. This substance (100 kilos.) is powdered and gradually added to crystallised sodium sulphide (90 kilos.) in water (60 kilos.) at 110°.

The mixture is heated at 120° until the organic compound becomes soluble. The solution is diluted, acidified with hydrochloric acid, and the yellow precipitate collected. The final product, which is soluble in aqueous alkali hydroxides or sulphides, gives on cotton yellow shades which are fast to scouring agents and acids; it is almost insoluble in concentrated sulphuric acid.

Thion yellow G, GG, GN (*K. D. R. P.* 139429; *D. R. P. Anm. K.* 24649; *Eng. Pat.* 16932, 1902; *Fr. Pat.* 323490). Tolylene-2:4-diamine and sulphur interact, forming a thio derivative (m.p. 145°), which when dissolved in hot aqueous sodium sulphide furnishes a yellow colouring matter precipitated by carbon dioxide from the alkaline solution.

The aromatic *m*-diamines yield complex thiocarbamides when heated with carbon disulphide (*Ber.* 1885, 18, 3293), and these thio derivatives when heated with sulphur at 150°-170° give rise to similar yellow dyes which are dissolved in aqueous sodium sulphide. Benzidine is sometimes added during fusion (*M. D. R. PP.* 152027, 153916, 166864; *A. ibid.* 171871). Tolylene-2:4-diamine itself yields a yellow dye when fused with benzidine and sulphur at 190°-280°, the product being rendered soluble by sodium sulphide (*M. D. R. P.* 163143; *T.M. D. R. P.* 163001).

Immedial orange C, N (*C. D. R. P.* 152595; *Eng. Pat.* 11898, 1902; *Fr. Pat.* 321183). Tolylene-2:4-diamine (50 kilos.) and sulphur (125 kilos.) are heated in an iron pan with stirrers until hydrogen sulphide is no longer evolved, and the product baked at 250° until a hard brittle mass is produced, which is then added to sodium sulphide (150 kilos.) at 110°-120°. The mixture is dissolved in water, and the colouring matter precipitated by acid. Cotton is dyed in orange-brown shades which are brightened by hydrogen peroxide, but scarcely affected by chromic acid.

This colouring matter is insoluble in concentrated sulphuric acid.

Eclipse yellow G, 3G (*G. D. R. PP.* 138839, 145762, 145763). When heated with commercial formic acid in a reflux apparatus, tolylene-2:4-diamine gives rise to formyltolylene-2:4-diamine, very sparingly soluble pyramids, m.p. 113°–114°, and diformyltolylene-2:4-diamine, acicular aggregates, m.p. 176°–177°. These products, which are separated by fractional crystallisation from water, the latter being the more soluble, are both used in the preparation of sulphide dyes. The formyl derivative is added to a solution of an equal weight of sulphur in 3 parts by weight of crystallised sodium sulphide fused in its water of crystallisation and the temperature raised to 240°. The dye, which is obtained as a light brown precipitate on acidifying a solution of the fusion, gives bright yellowish-orange shades, those from the monoformyl derivative having the browner tint. The thionation may also be effected by sulphur, either alone or with the addition of benzidine or other analogous bases. The formyl derivatives may be replaced by the condensation products of tolylene-2:4-diamine and oxalic acid (*M. D. R. PP.* 156177, 157103).

The yellow dye obtained by thionating diformyltolylene-2:4-diamine (*D. R. P.* 138839) contains no oxygen, and shows little evidence of free amino groups; it is regarded as a complex polysulphide $(C_{17}H_{12}N_4S_2)_6(S\cdot SH)_5(S\cdot S\cdot SH)_5$ oxidising with alkaline permanganate to a sulphonic acid $(C_{17}H_{12}N_4S_2)_6(SO_3H)_{10}$ (*Chem. Soc. Trans.* 1920, 117, 833).

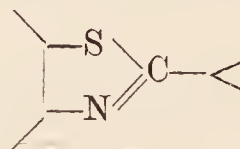
Similar sulphide yellows are produced by fusing with sulphur at 200°–220° mixtures of tolylene-2:4-diamine and its diformyl derivative or diformylbenzidine (*G. D. R. PP.* 146917; *A.* 159097, 170746), and various shades of yellow, yellowish-brown, and orange are obtained by employing mixtures of tolylene-2:4-diamine and various aromatic nitro-derivatives, such as the nitranilines and their homologues, and the dinitro-benzenes and -naphthalenes (*By. D. R. PP.* 201834, 201835, 201836).

Immedial yellow GG (*C. D. R. P.* 180162; *Eng. Pat.* 4097, 1906; *Fr. Pat.* 372137; *U.S. Pat.* 892455). The relationship between sulphide yellows and thiazole dyes is illustrated by the employment of dehydrothiitoluidine (*v.* PRIMULINE) in the sulphur fusion. Benzidine (19 parts), dehydrothiitoluidine (16 parts), and sulphur (70 parts) are heated together for 1 hour at 210°, and the product digested with fused sodium sulphide at 120° until rendered soluble. The dye is then precipitated by a mineral acid. Cotton is dyed in greenish-yellow shades very fast to scouring agents (*cf.* *B. Rassow*, *D. R. P.* 234638).

Among the numerous other yellow sulphide dyes are **Thioxine yellow** and **Thioxine orange**, yellowish powders slightly soluble in concentrated sulphuric acid and insoluble in sodium hydroxide; **Thionol yellow G, R**; **Thionol orange**; **Thiogene yellow G, GG, 5G**.

Reference has already been made to the employment of carbazole in the production of sulphide blues and blacks. Its N-substituted derivatives, the alkyl, aryl, or aralkyl carbazoles, when heated with sulphur, preferably in the presence of benzidine, toluidine, or another of

sulphide yellow intermediates, give rise to thionated yellow dyes very fast to chlorine (*C. D. R. P.* 475014). Similar yellow colouring matters are produced by the sulphur fusion of mixtures of aromatic bases containing methyl or other alkyl groups, or formyl radicles (*U.S. Pat.* 1140745; *Eng. Pat.* 4035, 1915; *D. R. P.* 302792). The presence of these groups supports the view that yellow sulphide dyes are complex thiazole derivatives containing the chromophor

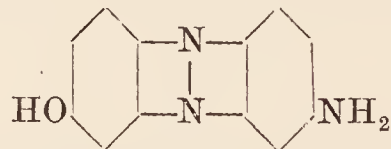


Providing that alkyl groups are present, sulphonic or carboxylic acids of the benzene, diphenyl, or naphthalene amines, for instance, ethyl- α -naphthylamine sulphonic acids, are amenable to the sulphur fusion yielding yellow, orange, and brown dyes (*D. R. P.* 205104).

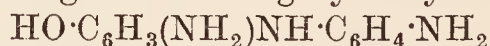
REDDISH SULPHIDE DYES.

Although bright red sulphide dyes have not yet been obtained, it has been found possible to produce various shades of purple, violet, and maroon by thionating certain red colouring matters. In these reactions sulphur is probably introduced into the molecule without destroying the complex to the presence of which the red colour is due.

Immedial maroon, bordeaux, and violet (*C. D. R. P.* 126175; *Eng. Pat.* 14836, 1900; *Fr. Pat.* 303107; *U.S. Pat.* 701435). **Thionone brilliant scarlet LR** (*L. B. H.*); **Thionone corinth B** (*L. B. H.*). The simplest starting material for the production of the bordeaux-red sulphide dyes is 6-amino-3-hydroxyphenazine



prepared by reducing with iron and acetic acid 2:4-dinitro-4'-hydroxydiphenylamine (from *p*-aminophenol and chloro-2:4-dinitrobenzene) and oxidising the resulting hydroxytriamine



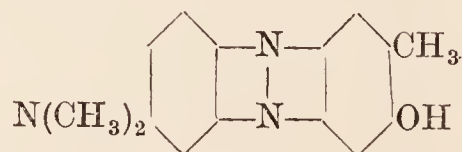
in alkaline solution with manganese dioxide.

The sulphonic and carboxylic acids of this phenazine, which are obtained in a similar manner, are also employed in the sulphide fusion.

Tolylene red (neutral red), 6-dimethylamino-3-amino-2-methylphenazine



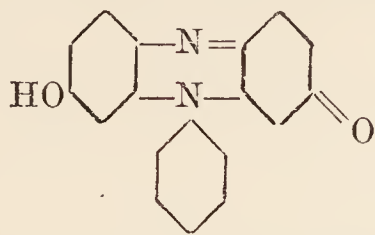
obtained by oxidising a mixture of dimethyl-*p*-phenylenediamine and tolylene-2:4-diamine, is too insoluble for employment in the sulphide fusion, and is converted either into its sulphonic acid by fuming sulphuric acid (23 p.c. SO_3) or into the corresponding hydroxy-azine



by hydrolysis with water under pressure.

These products being soluble in aqueous alkali hydroxides or sulphides are utilisable in the production of reddish sulphide dyes.

Safranol. 3-Hydroxy-6-oxy-N-phenylphena-

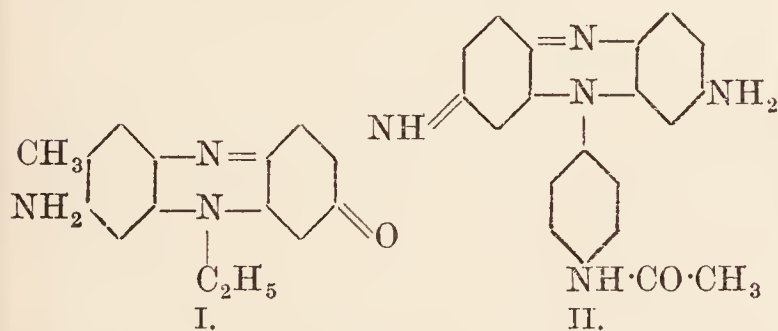


zine produced either by condensing nitrosophenol with *m*-hydroxydiphenylamine, by oxidising this base mixed with *p*-aminophenol or by the alkaline hydrolysis of phenosafranin or phenosafraninone, is employed in the sulphide fusion, as is also phenosafranin and its carboxylic and sulphonic acids.

One of the foregoing azines (10 parts) is added to a solution of sulphur (20 parts) in sodium sulphide (50 parts) and water (10 parts), and the mixture heated to 140°–150° until the product dissolves in water to a dark violet solution. This operation may also be carried out either in a reflux apparatus or in an autoclave. The sulphide dyes from 6-amino-3-hydroxyphenazine and its carboxylic and sulphonic acids, and from the alkali soluble tolylene red derivatives give brownish-violet shades, the safranol condensation product dyes in bluish-violet tints, whereas reddish-violet shades are obtained from the dyes derived from N-ethylsafranin and from phenosafraninone and its carboxylic and sulphonic acids.

The fusion of these phenazine derivatives is also carried out in the presence of metallic salts (CuSO₄, CoSO₄, or NiSO₄, *cf.* *Lev.* Eng. Pats. 24008, 1906; 17749, 1907), the resulting dyes being redder and faster than those produced in the absence of these adjuvants.

3-Amino-6-hydroxyphenazine and its C-methyl homologue when heated to 120°–140° with aqueous sodium polysulphide and copper sulphate or metallic copper give dark red sulphide dyes. Safraninone and safraninone when similarly treated yield violet-red colours and N-ethyl-2-methylsafraninone (I.)



gives rise to a bordeaux-red dye. *p*-Acetylaminosafranin (II.) (N-acetylaminophenyl-3 : 6-diaminophenazine) and its homologues when heated at 120° for 20 hours with aqueous sodium polysulphide containing copper sulphate give rise to bluish-violet dyes precipitated by acid, which are faster and brighter than those prepared from the simpler safranines (*M.* D. R. PP. 171177, 177709, 179021, 222418; *Fr.* Pat. 361608; *U.S.* Pat. 818980).

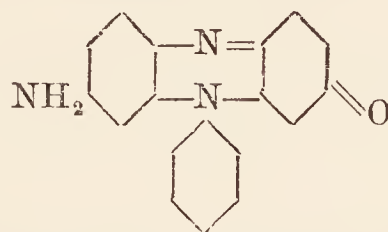
Azines without hydroxyl groups, such as tolylene red, being insoluble in alkali sulphides, are first fused with sulphur at 180°–230°, the

product being then treated with sodium sulphide at 180°. Cotton is dyed in reddish-brown shades (*B. D. R. P.* 147990).

Thionol purple 2B (*Lev. B. D. C.*), a reddish-purple dye of good fastness, is manufactured by thionating, either with or without a copper salt, the oxidation product of the indophenol from *p*-nitrosophenol and *m*-tolylenediamine formaldehyde bisulphite. The copper salt may be replaced by cobalt or nickel salts (*Eng. Pats.* 24008, 1916; 17749, 1917; *Vlies, J. Soc. Dyers Colourists*, 1913, 29, 318).

Thiogen purple (*M. D. R. P.* 181125; *Eng. Pat.* 2797, 1906; *Fr. Pat.* 372277; *U.S. Pat.* 829740). The N-alkylated aminohydroxyphenylphenazines and their tolyl homologues, the chloro derivatives of the azines (produced from chloroaminophenols) when heated at 110°–135° in a reflux apparatus or under pressure with aqueous or alcoholic sodium polysulphide give sulphide colouring matters dyeing cotton in clear bordeaux-red shades, the higher the temperature of the fusion the bluer the tint produced. Reddish-violet and dark red sulphide dyes are obtained by heating in a reflux apparatus at 110°, the chloro- and bromophenazines and the corresponding halogenated toluidines with aqueous sodium polysulphide in the presence of copper sulphate (*M. D. R. P.* 174331; *A. ibid.* 207096). In these condensations the halogen radicle of the chloro- or bromo-azine is readily replaced by a SH group, and accordingly the organic base is first heated with sodium sulphide alone at 110°–140°, and subsequently treated with polysulphide at a high temperature. When the latter operation is omitted, intermediate mercaptan derivatives of the hydroxyphenazines are produced which have only a slight affinity for the cotton fibre and are converted into sulphur dyes by fusion with alkali polysulphide (*M. D. R. PP.* 181327, 187868; *Fr. Pat.* 360437).

Thiogen violet V, B (*M. D. R. PP.* 168516, 177493, 179960, 179961). Phenosafraninone, 3-oxy-6-amino-N-phenylphenazine (10 parts)

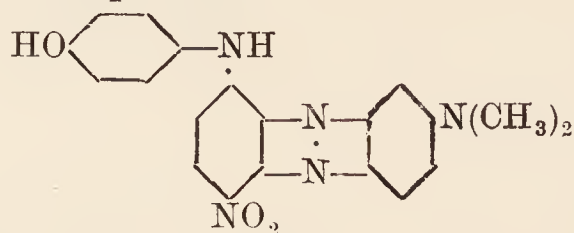


warmed at 115°–120° with sulphur (30 parts), alone or with a diluent, then heated further to 200°, and mixed with sodium sulphide. The violet dye produced, which contains sulphur, is converted into a colouring matter, dyeing bluer and faster shades by heating for 20 hours in a reflux apparatus at 135° with twice its weight of aqueous sodium polysulphide. The addition of copper sulphate or copper to the foregoing polysulphide fusion leads to the production of redder and faster shades of violet, the redness increasing with the amount of copper employed in the condensation.

Violet to violet-blue shades of sulphide dyes are produced by heating at 170° for 3 hours safranin (10 parts), sulphur (30 parts), and aniline (10 parts), or some other organic solvent of high boiling-point (*e.g.* dimethylaniline, benzidine). Bluer and more sombre tints are obtained either by prolonging the heating or by raising

the temperature to 240° (*M. D. R. P.* 178982; *Fr. Pat.* 360437).

Thion violets (*K. D. R. PP.* 144157, 152373, 160790, 160816, 165007). 4-Nitro-2-amino-4'-hydroxydiphenylamine and nitrosodimethylaniline hydrochloride condense to form the complex azine 1-nitro-4'-*p*-hydroxyphenylamino-6-dimethylaminophenazine



This condensation product (8 parts), heated at 130°–140° for 2–3 hours with sodium sulphide (40 parts) and sulphur (16 parts), yields a violet sulphide dye dissolving in water to a dark green solution, and in concentrated sulphuric acid with a bluish-green coloration.

Trihydroxyphenylrosinduline is obtained by the condensation of *p*-aminophenol and benzene-azo- α -naphthylamine hydrochloride, or from the former compound and α -nitronaphthalene (*K. D. R. PP.* 158077, 158100, 158101, 160789, 160815, 163239). This rosinduline (52 parts), heated for 5 hours at 160°–170° with sodium sulphide (160 parts), sulphur (40–60 parts), sodium hydroxide (40°Be., 24 parts), and water (200 parts), gives rise to a reddish-violet dye dissolving in concentrated sulphuric acid to a blue solution.

The indophenol from *p*-aminophenol and *p*-xylenol when heated with aqueous sodium polysulphide in a reflux apparatus for 16 hours or under pressure (125° for 12 hours), or in alcoholic solution for 2–3 days, gives rise to a sulphide violet which separates from solution in small brown crystals having a metallic lustre. This colouring matter dissolves in aqueous sodium sulphide to a blue solution, and dyes in deep violet shades which are very fast and, hitherto, unsurpassed in intensity (*C. D. R. P.* 191863; *Eng. Pat.* 4653, 1902; *Fr. Pat.* 318577).

Thiogene dark red GR (*M.*). 2:4-Dinitro-2'-hydroxydiphenylamine, produced by the condensation of 2:4-dinitrochlorobenzene and *o*-aminophenol, is heated under reflux with aqueous sodium polysulphide and copper sulphate for 24 hours. The dye, which is precipitated by air from the filtered aqueous solution, dyes in reddish-brown shades fast to washing (*Eng. Pat.* 14746, 1907 *Fr. Pat.* 379416; *D. R. P.* 194198).

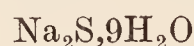
MANUFACTURE OF SULPHIDE DYES.

The apparatus most generally employed in the polysulphide fusion is a cylindrical cast-iron jacketed pan about 3 ft. deep by 2 ft. in diameter, and having a capacity of about 100 gallons. The jacket serves for the introduction of superheated steam, a pressure of 4–6 atmospheres sufficing to raise the temperature of the fusion to 125°–135°. The pan is fitted with a mechanical stirrer and its domed lid contains a man-hole for introducing the reagents, a thermometer tube dipping into the fusion, an opening leading to the reflux condenser, and an inlet tube for air under in-

creased or decreased pressure. The jacket is fitted with a manometer, and if the pan is to be used for fusions under pressure, it is also fitted with a pressure gauge. This plant serves for the majority of modern sulphide fusions (*e.g.* dinitrophenol black), which are carried out at temperatures only slightly above the boiling-point of water (105°–120°). In fusions requiring higher temperatures (*e.g.* 200°–300°, cachou de laval, eclipse brown, &c.) smaller cast-iron pans are employed, heated either by direct fire or in an oil bath, the fittings of the melting-pan being similar to those of the jacketed pan. Vaseline or a high-boiling liquid (*e.g.* aniline, b.p. 182°) may be employed in the oil bath, which is preferable to heating by direct fire, as local overheating is avoided. This mode of heating is employed both in sulphide melts and in fusions with sulphur alone in the production of yellow.

Sulphur fusion.—This fusion is restricted chiefly to the production of sulphide yellows, oranges, and browns, which, being allied to the thiazole dyes (*v.* PRIMULINE), are prepared in a similar way. A few bases give blue and black sulphide dyes with sulphur alone at comparatively low temperatures, 2:4-diaminophenol, for instance, with sulphur at 80°–120°, gives a colour dissolving in sodium sulphide to a blue solution, and dyeing cotton in bronzy black shades, which, however, are not fast to chroming (*Vidal, Eng. Pat.* 16449, 1896). The products of the sulphur fusion for yellows are insoluble substances, which are ground up and rendered soluble by boiling with concentrated aqueous sodium sulphide.

Sulphide fusion.—The heating of nitro compounds and sulphur is avoided, so far as possible, owing to the risk of explosion, and in general the sulphide fusion is carried out with a mixture of sodium sulphide and sulphur (sodium polysulphide $\text{Na}_2\text{S}_2 \dots \text{Na}_2\text{S}_6$) generally in the presence of water either added or derived from the commercial crystallised sulphide



In the case of nitro compounds yielding easily decomposable polyamines on reduction, it is preferable to add the organic substance to the fused polysulphide rather than to reduce the nitro compound with sodium monosulphide before introducing the sulphur.

In the Vidal black process the *p*-aminophenol produced by reduction from *p*-nitrophenol is comparatively stable, and consequently the sulphur can be added after reduction. With dinitrophenol, however, the best result is obtained by adding the nitro compound to the polysulphide in aqueous solution when reduction and thionation occur concurrently. The black obtained by reducing dinitrophenol with aqueous monosulphide, and then adding sulphur, is distinctly inferior in tinctorial properties to Cross dye black BX (*H.*).

At high temperatures sodium monosulphide will act as a thionating agent, for, on reducing nitro compounds, it becomes itself converted into a complex mixture of sulphites, polysulphides, and thiosulphates. A sulphide brown is produced by fusing dinitrophenol at 160°–180° for 6–8 hours with crystallised sodium sulphide.

The fusion under reflux condenser, which is employed when the formation of colour occurs

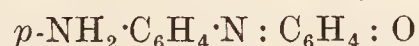
at temperatures near 100° , is of great utility in the manufacture of blacks from dinitrophenol, picric, and picramic acids, 2:4-dinitro-4'-hydroxydiphenylamine and its chloro derivatives and especially in the production of blues from indophenols, and of violets from hydroxy and amino derivatives of the azines.

Alcoholic condensation.—The thionation is often carried out in alcoholic solution, the sulphide employed being either anhydrous or crystalline. In this medium sulphur dissolves readily to an extent corresponding with the tetrasulphide Na_2S_4 . Although on account of the low temperature (80°) the condensation takes a long time, yet the products are obtained in a very pure condition, the dyes derived from certain indophenols separating in a crystalline form. The alcoholic or aqueous fusions are sometimes effected under pressure. Immedial black, when prepared in this way from 2:4-dinitro-4'-hydroxydiphenylamine or its reduction products, separates as a crystalline dark blue lustrous powder dyeing in very intense black shades.

Additions to the sulphide fusion.—Sometimes the temperature of the condensation is raised either by substituting amyl alcohol for water or ethyl alcohol, or by adding to the fusion such inert substances as glycerol, naphthalene, or β -naphthol. Aromatic amines have also been added to sulphide fusions, but in some cases they take part in the condensation. Benzidine, for example, is frequently added to sulphur fusions for yellow. Dehydrothiotoluidine, when melted with sulphur alone, gives no colouring matter, but when benzidine is introduced into the melted mixture immedial yellow GG is produced (C. D. R. P. 180162).

Copper is added to many sulphide fusions, most frequently in the form of sulphate, but also as copper bronze; it imparts greenish shades to black, reddish shades to browns and violets, and yellowish shades to red. In some cases this metal alters the chemical properties of the dye without greatly modifying its shade of colour. The immedial black fusion in presence of copper gives a greenish instead of a bluish-black, which, unlike ordinary immedial black, is not oxidised on the fibre by hydrogen peroxide to immedial blue. It is often immaterial whether the copper is added during thionation or afterwards. Zinc salts are added to fusions of 1:8-naphthalene derivatives to prevent the formation of brown impurities during the preparation of certain blue sulphide dyes (By. D. R. P. 116655).

The condensation of the indophenol



with aqueous polysulphide does not give a satisfactory colour unless manganous sulphate is added to the fusion when an indigo blue dye is produced (P. D. R. P. 22406; Fr. Pat. 406225).

The course of the sulphur and polysulphide fusions may be ascertained by dissolving samples in water or sodium sulphide, and precipitating the sulphide dye and excess of sulphur with dilute acid. The acid filtrate contains the unthionated amines which may be recognised in one of three ways: (1) By diazotisation and coupling with alkaline β -naphthol; (2) oxidation to indophenols; (3) production of coloured

solutions: this occurs in the case of the azines and other coloured bases. The fusion product is dissolved in water, or if necessary, aqueous sodium sulphide, and in some cases (*e.g.* dinitrophenol black) the colour is precipitated from the filtered solution of its leuco derivative by passing in a current of air. This precipitation by air sometimes takes place, however, with considerable difficulty, and then the colouring matter is precipitated by dilute acid in a wooden vat surmounted with an efficient draught hood for carrying off the torrent of hydrogen sulphide set free when the alkali sulphide solution is acidified. In other cases the dye is salted out with sodium, ammonium, or calcium chloride, or other soluble salts. The precipitated dye is collected either in a filter press or on a vacuum filter, the latter being employed only when the precipitate is not too slimy.

Immedial pure blue is purified either through the soluble bisulphite compound or by dissolving the leuco derivative of the colouring matter in hydrochloric acid, filtering from insoluble impurities and precipitating the hydrochloride of leuco immedial pure blue by the addition of brine solution.

THE DYEING OF SULPHIDE COLOURS.

The sulphide dyes are best dissolved in wooden vessels by pouring over them boiling water containing sufficient sodium sulphide to bring the colours into solution. Copper or brass vessels are to be avoided, and the metallic parts of the dyeing apparatus should consist of iron or lead. The dyeing operation is carried out in wooden or iron vats heated by steam coils. In addition to sodium sulphide, the bath is generally prepared with sodium carbonate and either sodium chloride or sulphate. In the following dyeing recipes the percentage of ingredients is always reckoned on the weight of dry cotton, which is generally dyed in about 20 times its weight of water.

Sulphide blacks.—For dyeing 100 grms. of cotton yarn in a full shade of cross dye black BX (H.), 10 grms. of this colour are dissolved in 500 c.c. of hot water containing 20 grms. of crystallised sodium sulphide and 5 grms. of sodium carbonate. This mixture is boiled for 5 mins., the solution made up to 2 litres, the yarn, which has been previously well boiled out with water, is then introduced, and the bath kept boiling for 15 mins. This temperature is maintained for 30 mins. longer, during which period 75 grms. of salt are gradually added, the bath being kept up to constant volume by the addition from time to time of hot water. The dyed yarn is then lifted and rinsed in cold water.

Although after-chroming does not materially alter the shade of black which is fully developed as the result of aerial oxidation, nevertheless this treatment is sometimes used to increase the fastness of the dye, and is effected by immersing the rinsed yarn for 30 mins. at 60° in 2 litres of water containing 2 p.c. of sodium or potassium bichromate, and 2 p.c. of sulphuric acid. Any bronziness due to oxidation or excess of colour is removed and the tone of the black improved by heating the dyed yarn for 30 mins. at 60° with the following emulsion: 5 p.c. of soap, 1.5 p.c.

of olive oil, and 1.0 p.c. of ammonia in 2 litres of water. The finished yarn is then squeezed out and dried without washing.

The dyeing process for Vidal black (*P.*) from *p*-nitrophenol is carried out as above with 10–15 p.c. of the colour, but in this case, after-chroming is essential in order to develop the full shade of black from the dark green tints produced by aerial oxidation. The above-described finishing process enhances the tone of black obtained by chroming.

Immedial black V extra (*C.*) is dyed in full shades with 15–25 p.c. of colour, 10–18 p.c. of crystallised sodium sulphide, and for each 10 gallons of liquor are added 4.5–8 ozs. of sodium carbonate and 1–3 lbs. of common salt or anhydrous sodium sulphate. The yarn is dyed at a boiling temperature for 1–1½ hours and rinsed in water, containing 4.5–8 ozs. of sodium formate or acetate per 10 gallons of liquor. For grey shades only 1–8 p.c. of this black is required, with 2–6 p.c. of sulphide crystals, one-third the amount of salt or sodium sulphate, and the same proportion of sodium carbonate as for full black shades.

Thiogene black conc. (*M.*) and thioxine black RNO (*O.*) are dyed in full shades with 10 p.c. of colour, 30 p.c. of crystallised sodium sulphide, 8–10 p.c. of dry sodium carbonate, and 50 p.c. of common salt or anhydrous sodium sulphate. The bath should have at 15° a sp.gr. of 6.7°Bé. Cotton yarn is dyed at the boil for 1 hour, and mercerised yarn at 90° for a somewhat longer period.

An increase in fastness and depth of the sulphide blacks is produced by an after-treatment with 1–2 p.c. of chrome alum or copper sulphate, 1.5–2 p.c. of potassium bichromate, and 5 p.c. of acetic acid.

Sulphide blues.—Immedial indone 3B is dyed on cotton yarn in pale and medium shades by using 2–10 p.c. of colour, 5–20 p.c. of sulphide crystals, and 2–10 p.c. of glucose with 4.5–8 ozs. of soda ash and 1 lb. of common salt or dry sodium sulphate to each 10 gallons of water. Deeper shades are obtained with 10–16 p.c. of colour, and correspondingly greater amounts of sodium sulphide and glucose. The lighter shades are dyed at 30°–40°, and the darker at 60°–80°, a brighter tone being thus obtained than at the boiling temperature.

Thiogene deep blue and thiogene cyanine B are dyed in full shades with 6–10 p.c. of colour, 10–15 p.c. of sulphide crystals, 5 p.c. of sodium carbonate, and 30 p.c. of sodium chloride at a boiling temperature for 1 hour.

Sulphide greens.—Immedial green is dyed on cotton in full shades with 14 p.c. of colour, the same proportion of sulphide, 0.5 p.c. of soda ash, and 5 p.c. of common salt or dry sodium sulphate. The tint is brightened by exposure to air after rinsing, or by warming the dyed yarn with soap solution containing sodium carbonate.

Sulphide yellows.—Thiogene yellow 5G and thioxine yellow G require for the dyeing solution from 2 to 4 times their weight of sulphide crystals; the bath is prepared with 4–5 p.c. sodium carbonate, 25–35 p.c. of sodium chloride, or 15–20 p.c. of dry sodium sulphate, the dyeing being effected just below the boiling-point. Immedial yellow GG is dyed at 70°–80° without sodium chloride or sulphate.

Sulphide browns.—These colouring matters dissolve with 0.4–1.0 part by weight of sulphide crystals, and are dyed for 1 hour at the boil with sodium carbonate and sodium chloride, full shades being obtained with 8–10 p.c. of colour. The fastness of sulphide browns to light, washing, milling, and alkalis is very satisfactory, but they are appreciably affected by chlorine or hypochlorites.

Sulphide violets and purples.—The maroons, violets, purples, and bordeaux of this series are best dyed at 60°–80°, and not at boiling temperatures. In some cases sodium chloride or sulphate is not added to the bath, but a little glue (one-fifth of the weight of dye) is introduced with the object of brightening the shade.

Sulphide colouring matters as vat dyes.—Immedial blue is reduced with alkaline hydrosulphite until the solution assumes a brownish-yellow colour, the cotton is then introduced, and the colour developed on the fibre by oxidising agents. Indigo can be dyed from the same bath. The sulphide dyes cannot be employed in the zinc-dust or alkaline ferrous sulphate vat, because they yield insoluble lakes with the metallic radicles present (*M. D. R. P.* 146797; *Eng. Pat.* 24455, 1899; *Fr. Pats.* 295589, 301740; *U.S. Pat.* 680472; *cf. Fr. Pats.* 299733, 385087).

Various brands of sulphide black (*e.g.* kryogen black and thiophenol black) have been dyed on cotton from a fermentation vat, although the process is unserviceable for the animal fibres (*B. D. R. P.* 200391; *Eng. Pat.* 12219, 1907; *Fr. Pat.* 379584).

Dyeing of sulphide dyes on wool, silk, and fibres other than cotton.—The destructive action of the alkali sulphide on wool and silk is mitigated by adding to the dye-bath an amount of dextrose equal to twice the weight of sodium sulphide present. Silk is dyed for 1 hour at 80° in 20 times its weight of liquor, each litre of which contains 20–30 grms. of sulphide black, or 5–10 grms. of some other sulphide colour, 1 gm. of sodium carbonate, 5–10 grms. of Glauber salt, 3 c.c. of Turkey-red oil, and the minimum amount of sodium sulphide with twice its weight of dextrose (*C. D. R. P.* 159691).

Wool is dyed at 60° in a similar bath, but without the Turkey-red oil. Tannin may be employed as the protective agent instead of dextrose. A preliminary treatment of wool with warm 4 p.c. formaldehyde solution protects the fibre from the action of alkali sulphides (*Kann, D. R. PP.* 144485, 146845; *Eng. Pat.* 25971, 1906); but wool thus treated, although taking up sulphide dyes (*e.g.* cachou de laval) in moderately alkaline baths at 90°, is not dyed by sulphide colours in colder baths of moderate alkalinity (*Levinstein, J. Soc. Dyers.* 1907, 296; *Eng. Pats.* 25971, 1906; 19840, 1907). The addition of ammonium chloride or alkali bisulphite lessens the destructive action of alkali sulphides on wool and silk (*Bl. D. R. P.* 130848).

Artificial silk is readily dyed by sulphide colours even at comparatively low temperatures, 30°–40° for light shades, and 60° for heavy shades, in the latter case the bath being prepared with sodium sulphate and sodium carbonate. Ramie and hemp fibres are readily dyed by sulphide colours, jute absorbs these dyes less easily than the cotton fibre.

CONSTITUTION OF SULPHIDE DYES.

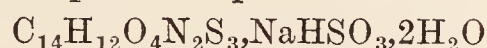
The problem of ascertaining the constitution of the sulphide dyes is greatly complicated by the uncrystallisable nature of these products, and by the circumstance that these dyes, like many other substantive colours, tend to form colloidal solutions which render impossible the determination of their molecular weight.

The commercial sulphide dyes contain generally colloidal sulphur and a labile form of the element 'thioxone sulphur.' There is mutual adsorption between the dye and colloidal sulphur.

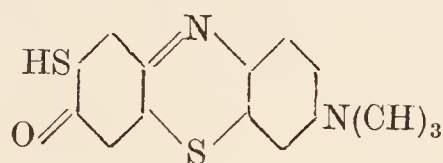
A sulphide dye purified from colloidal and thioxone sulphur—often 20–25 p.c. of the total sulphur content—retains its solubility in aqueous sodium sulphide or hydrosulphite, but has appreciably inferior dyeing properties (Zänker, *Zeitsch. angew. Chem.* 1919, 32, 49).

Only in the case of the simplest members of the series, the sulphide blues, has it been found possible to obtain crystalline derivatives, and through these compounds to establish a relationship between the sulphide blues and the colours of the methylene blue series.

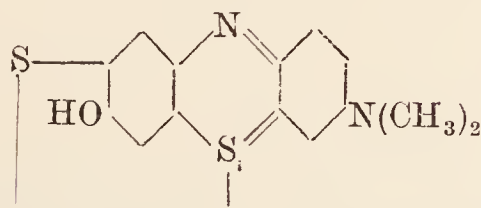
Immedial pure blue (C. D. R. P. 134947) gives a bisulphite compound



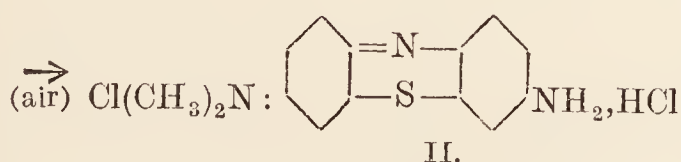
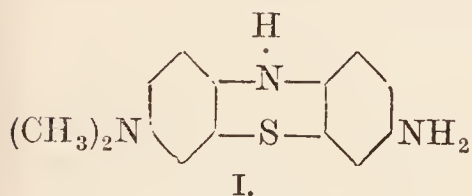
crystallising in yellow needles (D. R. P. 135952). The colouring matter contained in this additive compound has been given the following constitution, but probably immedial pure blue is the disulphide corresponding with the mercaptan represented by the first of these formulæ



or

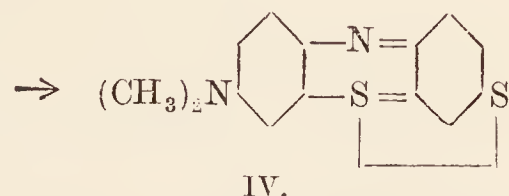
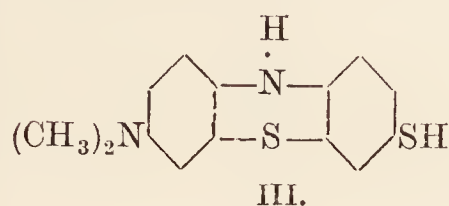


Gnehm and Bots (*J. pr. Chem.* 1904, [ii.] 69, 169) find, however, that the bisulphite compound is more correctly represented by the formula $\text{C}_{14}\text{H}_{12}\text{O}_2\text{N}_2\text{S}_3 \cdot \text{NaHSO}_3 \cdot 2\text{H}_2\text{O}$, a result which would indicate a somewhat different constitution for immedial pure blue. On heating methylene blue with alcoholic ammonia at 140° Gnehm and Kaufler (*Ber.* 1906, 39, 1016) obtained dimethyleucothionoline I.

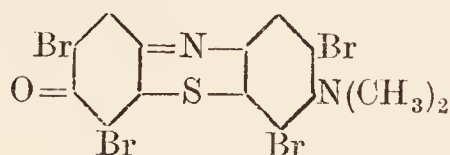


which became oxidised to dimethylthionoline (II.). The diazo compound of the latter was converted into the corresponding xanthate, and this substance hydrolysed with 80 p.c. sulphuric acid. The final product was an amorphous bluish-black powder, dissolving in aqueous

sodium sulphide to a colourless leuco compound, and dyeing cotton from this solution in greyish-blue shades. These results indicate that the replacement of NH_2 in dimethyleucothionoline by SH furnishes a leuco compound, having the constitution III., and accordingly the bluish-black substance, which has the properties of a sulphide dye, would probably be represented by the formula IV.

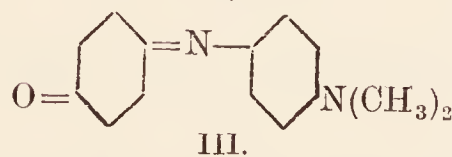
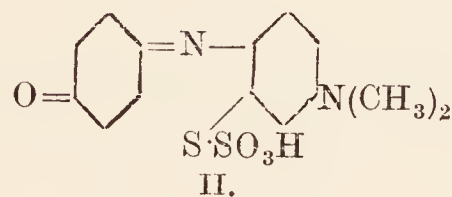
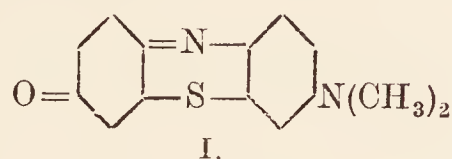


Moreover, immedial pure blue, when heated in sealed tubes with potassium chromate and hydrobromic acid, gives a 42 p.c. yield of tetrabromomethylene violet



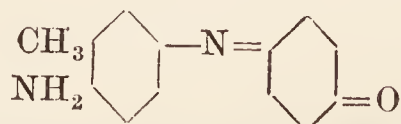
a substance which has also been produced synthetically from methylene blue (Gnehm and Kaufler, *Ber.* 1904, 37, 2618, 3032).

Methylene violet (I.) and the indophenol-thiosulphonic acid (II.), when treated below 140° with sodium tetrasulphide in aqueous or alcoholic solution, yield a blue closely analogous to immedial pure blue which is prepared from the indophenol (III.)



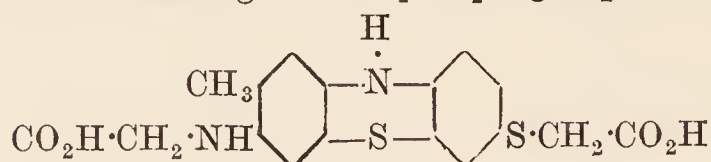
The similarity in the products of these two condensations points to the existence in the sulphide blues of the thiazine ring, which is present in methylene blue, but in addition the leuco derivatives of sulphide blue contain SH groups, which undergo oxidation to insoluble sulphide blues, which are to be regarded as complex disulphides.

Immedial indone, produced from the indophenol



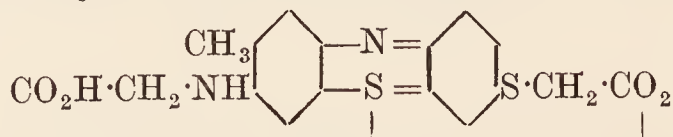
has been found by Frank to undergo condensation with chloroacetic acid, so that its leuco

derivative gives rise to a readily purified compound containing two $\text{CH}_2\cdot\text{CO}_2\text{H}$ groups

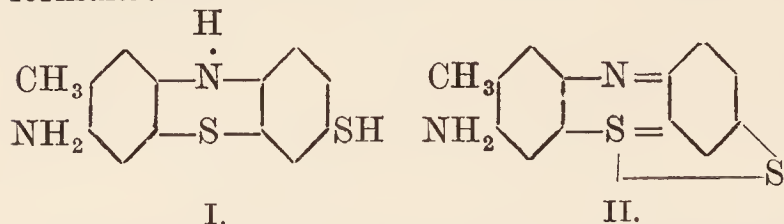


(Chem. Soc. Trans. 1910, 97, 2047).

This product is readily oxidised to a blue colouring matter, which, unlike the original immedial indone, has no affinity for cotton in a sodium sulphide bath, but dyes wool bright blue from an acid bath. This wool dye has probably the following constitution:—

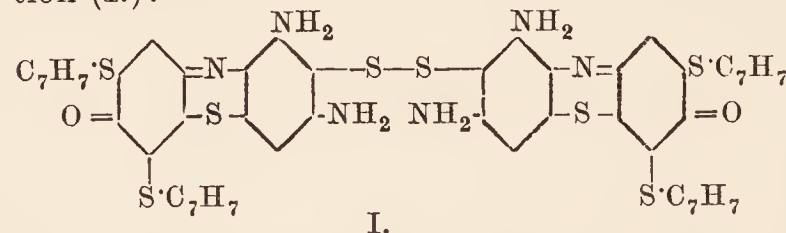


These results, therefore, indicate that the constitutions of leuco-immedial indone (I.) and of immedial-indone (II.) are most probably to be represented respectively by the following formulæ:—

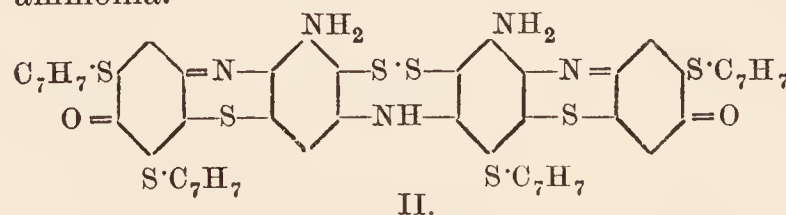


The alkylation of immedial black with benzyl chloride in the presence of aqueous sodium sulphide leads to the production of several substances which are separated by successive extraction with carbon disulphide, chloroform, and phenol and chloroform (D. R. P. 331758).

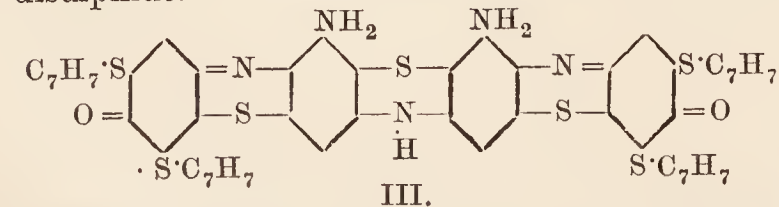
The substance soluble in carbon disulphide has the empirical formula $\text{C}_{52}\text{H}_{40}\text{O}_2\text{N}_6\text{S}_8$, and is regarded as having the following constitution (I.):—



A second product (II.), sparingly soluble in carbon disulphide, and extracted by chloroform, results from the foregoing by the elimination of ammonia.



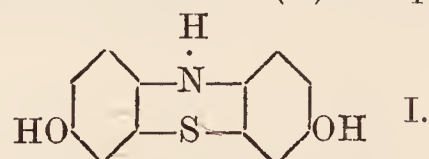
A third substance, insoluble in carbon disulphide and chloroform, is produced by eliminating ammonia from 2 molecules of the first product; and a fourth compound (III.), differing from the first in containing less sulphur and less nitrogen has also been isolated, being sparingly soluble in chloroform, although insoluble in carbon disulphide.



These results serve to indicate the relation-

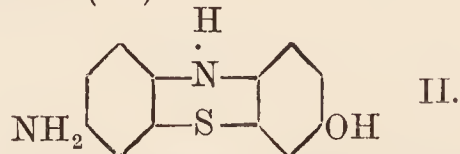
ship between the more complex sulphide blacks and the less condensed sulphide blues. They show, moreover, that in all probability the blacks are not homogeneous compounds, but mixtures of highly-condensed molecules (*cf.* Ris, Ber. 1900, 33, 796; D. R. P. 122850).

Vidal's earlier researches also point to the existence of thiazine rings in sulphide blacks (Mon. Scient. 11, 2, 655; 17, 427; D. R. P. 99039). On heating together quinol, sulphur, and ammonia, water and hydrogen sulphide were eliminated and leucothionol (I.) was produced



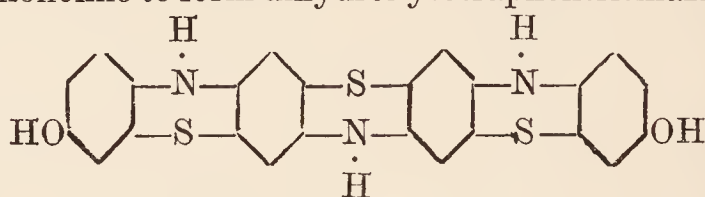
which is also formed together with a large proportion of black colouring matter by heating *p*-aminophenol and sulphur, and is obtained in quantitative yield by heating molecular proportions of *p*-aminophenol and quinol with sulphur.

Quinol and *p*-phenylenediamine, when heated with sulphur, give water, hydrogen sulphide, and leucothionline (II.)



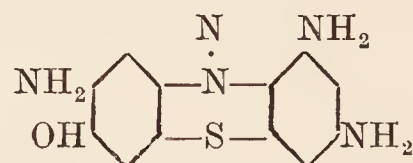
which on further heating with sulphur gives a black colouring matter.

Since leucothionol, on heating with sulphur and ammonia, also gives rise to a black dye, Vidal supposes that the black arises from a further condensation of leucothionol and leucothionline to form dihydroxytetraphentritiazine



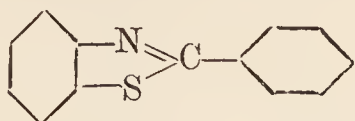
which he regards as being the essential constituent of Vidal black. This assumption does not, however, explain the characteristic mercaptan properties of the sulphide colours. It is evident that these colours must, in addition to the thiazine rings, contain mercaptan sulphur SH , or even polysulphide sulphur S_xSH in side chains.

2:4-Diaminophenol is readily converted by aqueous sodium polysulphide at 100° into diaminoleucothionline



which is easily oxidised to the corresponding diaminothionline, but without exhibiting any dyeing properties. When, however, diaminophenol is heated with aqueous thiosulphate, it passes into complex thiosulphonic derivatives, dissolving in aqueous alkalis to blue solutions, and dyeing cotton in blue shades. In the second thionation of diaminophenol, sulphur is introduced into the side chain as well as into the thiazine ring. The processes for preparing Clayton black are further examples of this type of condensation (D. R. PP. 120504, 120560, 136016; Eng. Pats. 21832, 22460, 1898; Fr. Pat. 288465).

The yellow and brown sulphide dyes resemble dehydrothiotoluidine and primuline in containing the thiazole group



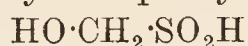
characteristic of the latter substances, and for this reason they are largely produced from tolylene-2:4-diamine, tolidine, and similar compounds containing carbon in side chains.

The sulphur of the thiazole ring is introduced by direct interaction of this element and the organic substance, giving rise to an insoluble coloured product which is rendered soluble by subsequent treatment with hot concentrated aqueous sodium sulphide. In the latter operation, mercaptan (hydrosulphide) groups are introduced into the molecule of the coloured substance, with the result that a true sulphide dye soluble in alkali sulphide solution is produced (*cf.* The Chemistry of the Sulphide Dyestuffs, F. M. Rowe, J. Soc. Dyers and Colourists, 1917, 33, 3).

Bibliography.—Friedländer, Die Fortschritte der Teerfarben-fabrikation (-industrie); Lunge, Die Schwefelfarbstoffe, Leipzig, 1912; Nietzke, Chemie der Organischen Farbstoffe; Schultz und Julius, Tabellarische Uebersicht der Kunstlichen Organischen Farbstoffen; Annual Reports, Colouring Matters and Dyes, Soc. Chem. Ind. Colour Index, Parts XX. and XXI.

G. T. M.

SULPHIFORMIN. Trade name for formaldehyde-sulphurous acid $\text{HO}\cdot\text{CH}_2\cdot\text{SO}_3\text{H}$, obtained by the interaction of formaldehyde, either in solution or as vapour upon gaseous or dissolved sulphur dioxide. The first action is the formation of formaldehyde sulfoxylate



which is slowly oxidised to formaldehyde sulphurous acid. Is a strong antiseptic. A 1 p.c. solution has been used for spraying vines (Malvesin, Bull. Assoc. Chim. Sucr. 1921, 38, 210).

SULPHINE *v.* PRIMULINE AND ITS DERIVATIVES.

SULPHOCYANIDES or **THIOCYANATES** *v.* CYANIDES.

SULPHOFORM. Trade name for triphenylstibine sulphide.

SULPHONAL *diethyldisulphonedimethylmethane* $(\text{CH}_3)_2\text{C}(\text{SO}_2\text{C}_2\text{H}_5)_2$ was first prepared by Baumann by treating dithioethyldimethylmethane or acetone mercaptol



with 5 p.c. potassium permanganate solution (Ber. 1886, 19, 2808).

It may also be prepared by heating diethyl disulphone methyl-methane $\text{MeCH}(\text{SO}_2\text{C}_2\text{H}_5)_2$ or diethyldisulphonemethane $\text{CH}_2(\text{SO}_2\text{C}_2\text{H}_5)_2$ with alcoholic potash and methyl iodide (Fromm, Annalen, 1889, 253, 147).

Some difficulty is experienced in preparing an odourless product. According to Kobbe, it is easy to determine whether a preparation is odourless or not by boiling 1 gm. with about 10 c.c. of water in a test-tube, when any remaining odour is easily detected (Kobbe, Pharm. Zeit. 1888, 730).

To isolate sulphon al from mixtures containing it, the mixture is evaporated to dryness,

extracted 3 times with its own volume of 90 p.c. hot alcohol, the extract on cooling is filtered and the alcohol distilled off. The residue is filtered while still hot, a few drops of potash added to the filtrate and treated 3 times with 3 times its volume of ether. The ether is then evaporated, the residue is dissolved in water and again treated with ether; on evaporation pure sulphon al is left (Vitali, Boll. Chim. Farm. 39, 461, 497).

Sulphon al begins to volatilise at 60° under ordinary pressure and is appreciably volatile with steam. Extraction with chloroform and evaporation of the solvent at a low temperature is recommended for the determination of sulphon al in its aqueous solution.

Sulphon al forms colourless, odourless, almost tasteless prismatic or foliated crystals, belonging to the monoclinic system and pseudo-rhombic in character. The habit of the crystals varies with the solvent in which they are grown (Seifers, Centr. Min. 1920, 97). Sulphon al may be identified as follows: it melts at 125.5° , volatilises at 300° , dissolves in 8 parts of boiling water, and 423 parts of water at 15° ; in 133 parts of ether at 15° ; 2 parts of boiling alcohol, 65 parts of alcohol at 15° ; and in 110 parts of 50 p.c. alcohol at 15° . 100 c.c. of benzene dissolve 8.01 grms., 100 c.c. of petroleum spirit 0.06 gm., and 100 c.c. of chloroform 32.5 grms. Toluene and acetone also dissolve considerable quantities of sulphon al (*cf.* Falck, Pharm. Zentr. 1919, 60, 409; J. Soc. Chem. Ind. 1919, 38, 962A). The sample should also be tested for sulphuric acid, potassium, and manganese. It is exceedingly inert towards all reagents, a characteristic property of the substance. Fused with potassium cyanide, it gives a smell of mercaptan. Mercaptan, according to Ritsert, may be formed by heating sulphon al with sodium-amalgam or pyrogallol. Fused with dry potash, a smell of mustard oil is evolved. Mercaptan is also formed by heating the substance with zinc chloride, sodium acetate, manganese dioxide, sodium amalgam, or with a fragment of charcoal; the white fumes which are at the same time given off turn litmus-paper red, and decolorise blue iodide of starch paper (J. Soc. Chem. Ind. 1888, 772; Kippenberger, Zeitsch. Nahr. Genussm. 1899, 2, 75). These tests, however, are said to be given by other compounds containing sulphur.

An odour of mercaptan is observed when 0.1 gm. of sulphon al or trional is fused with 0.1 gm. of sodium salicylate and the mass boiled with water; if 5 drops of alcohol and 5 drops of concentrated sulphuric acid are added, followed by a further 5 drops of the acid after one minute, and the mixture warmed, a turbid red-coloured solution is obtained, having an odour of methyl salicylate (Zimmermann, Apoth. Zeit. 1920, 35, 27).

By the following method 0.001 gm. may be detected. When sulphon al is heated moderately with 3 times its weight of powdered potash, an unpleasant smell is developed, the liquid becoming first yellow, then red; it becomes scarlet on cooling and changes to blue on addition of water, the liquid becoming turbid. On filtering and adding hydrochloric acid to the filtrate, the latter becomes violet, sulphur dioxide is evolved and sulphur is precipitated. In the

residue obtained by evaporating the acid solution to dryness, sulphate, hyposulphite and polysulphide may be detected in the usual way.

If the original mixture of sulphonal and potash be heated very strongly the red coloration changes to blue (Vitali, *l.c.*).

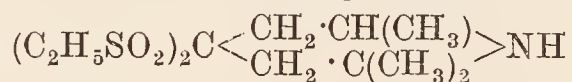
Sulphonal may be detected in trional and tetronal by treating the sample with ether in which sulphonal is much less soluble than the other two substances. The undissolved residue, if it contains sulphonal, can be detected by its m.p. 125.5°, its characteristic crystalline form and other reactions (Gabutti, J. Pharm. Chim. 1907, 25, 183).

Sulphonal is employed as a hypnotic, being intermediate in its action between chloral and paraldehyde and much safer than most drugs of its class as it does not depress the heart (Fischer, Pharm. Zeit. 33, 235).

Chlorosulphonal $\text{CH}_3(\text{CH}_2\text{Cl})\text{C}(\text{SO}_2\text{C}_2\text{H}_5)_2$ forms white pearly crystals, m.p. 78°–79° (Autenrieth, Ber. 1891, 24, 171).

Nitrososulphonal $\text{CH}_3(\text{CH}_2\cdot\text{NO})\text{C}(\text{SO}_2\text{C}_2\text{H}_5)_2$, rhombic tablets, has m.p. 104°–105° (Posner, *ibid.* 1899, 32, 1246).

Trimethylpiperidinediethylsulphonal



is obtained by oxidising the corresponding mercaptol with potassium permanganate in dilute sulphuric acid (Pauly, *ibid.* 1898, 31, 3149). It forms lustrous feathery crystals, m.p. 135°.

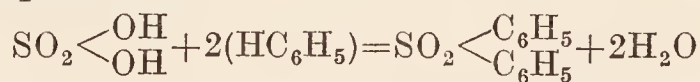
Sulphonal carboxylic acids are described by Posner (Chem. Zeit. 1905, 29, 1107).

Compounds in which the C_2H_5 group is replaced by some other radicle are formed from the corresponding mercaptan by similar methods to those used for preparing sulphonal (Stuffer, Ber. 1890, 23, 3228) (*v.* KETONES, also SYNTHETIC DRUGS).

SULPHONATED OILS (Turkey-red Oils), v. OILS, FIXED, AND FATS.

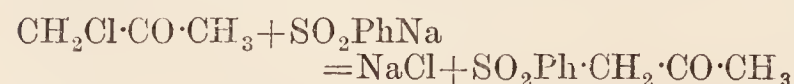
SULPHONATION. The operation of introducing the sulphonic acid group into a nucleus.

SULPHONES $\begin{matrix} \text{R} \\ \text{R}_1 \end{matrix} > \text{SO}_2$ may be obtained by heating aromatic hydrocarbons with fuming sulphuric acid:



Diphenylsulphone.

by oxidising vigorously the thioethers, or the sulphoxides, or the sulphides (Beckmann, J. pr. Chem. [ii.] 17, 439; Baumann and Walter, Ber. 1893, 26, 1124); by treating an alcoholic solution of sodium sulphinate or sodium alkylsulphinate with alkyl or alkylene halides (Otto, Ber. 1880, 13, 1272; *ibid.* 1888, 21, 652, 658; Annalen, 1894, 283, 181; *ibid.* 1895, 284, 300; Michael and Palmer, Amer. Chem. J. 6, 253) by the action of sodium alkyl sulphinate or mercaptide on chloracetone thus:



(Otto and Rössing, Ber. 1890, 23, 752); by the action of phosphoric anhydride at a high temperature on a mixture of an aromatic sulphonic acid and a hydrocarbon (Michael and Adair, *ibid.* 1877, 10, 583; *ibid.* 1878, 11, 116); by

the interaction of an aromatic sulphochloride and a hydrocarbon in the presence of aluminium chloride $\text{RSO}_2\text{Cl} + \text{R}'\text{H} = \text{HCl} + \text{RR}'\text{SO}_2$ (Beckurts and Otto, *ibid.* 2066); by the interaction of aromatic sulphinic acids and halogen derivatives of aromatic nitro compounds (Ullmann and Pasdermadjian, Ber. 1901, 34, 1150); a sulphone of formula $\text{C}_6\text{H}_5\text{SO}_2\text{C}_{10}\text{O}_7$, m.p. 121°, has been obtained by heating benzene sulphonic chloride with naphthalene and zinc-dust (Chrustschoff, Ber. 1874, 7, 1167), and di-*p*- and di-*o*-xylyl sulphones have been prepared by subjecting the well-cooled xylene to the action of sulphuric anhydride (Zorn and Brunel, Compt. rend. 1894, 119, 1224).

For other methods, see Otto, Ber. 1885, 18, 154, 246; *ibid.* 1891, 24, 1832; Stuffer, *ibid.* 1890, 23, 3226; Damköhler, J. pr. Chem. [ii.] 30, 321; Genvresse, Bull. Soc. chim. 1894, [iii.] 11, 501; Eng. Pat. 16333; J. Soc. Chem. Ind. 1899, 980; Blanksma, Pr. K. Akad. Wetensch. Amsterdam, 1901, 4 264; Posner, Ber. 1905, 38, 646.

The sulphones are isomeric with the organic alkyl sulphinates $\text{R} \cdot \text{SO} \cdot \text{OR}$, and form stable, neutral solid bodies not attacked by nascent hydrogen, hydrogen iodide, or by phosphorus pentachloride.

The sulphones of general formula $\text{R}_2\text{C}(\text{SO}_2\text{R})_2$ are stable towards alkalis, but when one of the groups SO_2Ph , SO_2Et , or Cl is introduced, they are decomposed by alkalis, the three sulphone groups being eliminated as sulphinic acid (Autenrieth, Ber. 1891, 24, 1512; Stuffer, *ibid.* 1890, 23, 1408). Diphenyl sulphone, when heated with sulphur at 250°–275° in a current of carbon dioxide, yields diphenyl sulphide, but many other sulphones do not react thus (Böesecken, Rec. trav. chim. 1911, 30, 137).

Sulphones containing one benzyl and another aromatic residue react with formaldehyde yielding diformal derivatives, but the presence of two aromatic residues without a benzyl group, or a benzyl group without a second aromatic residue, hinder this reaction (Fromm and Erfurt, Ber. 1909, 42, 3823).

Some of the disulphones $\text{R}_2\text{C}(\text{SO}_2\text{R})_2$ are employed in medicine (*v.* SULPHONAL, TRIONAL, TETRONAL). According to Baumann and Kast (Zeitsch. physiol. Chem. 14, 52; *ibid.* 1889, 15, 32; see also Laves, Arch. Pharm. 229, 448), the SO_2 group as such has no hypnotic effect and the sulphones containing the ethyl group are the most powerful, the methyl group having little or no effect.

But in the case of dimethyl disulphone dimethyl methane $\text{Me}_2\text{C}(\text{SO}_2\text{Me})_2$, the replacement of the methyl by the ethyl group produces no alteration in physiological properties, whilst the propyl, and to a less extent the *iso*-propyl, increases the activity. On the other hand, the introduction of a carbonyl group as in 2:2-diethyl disulphone pentane-3-one



destroys the hypnotic and all noxious properties (Hildebrandt, Chem. Zentr. 1905, ii. 502). The influence of other groups has also been studied by Hildebrandt.

For heterocyclic sulphones, *v.* Classz, Ber. 1916, 49, 350; *ibid.* 49, 614; *ibid.* 49, 1408; *ibid.* 49, 1880.

By the action of liquid sulphur dioxide on alkali iodides De Forerand and Taboury (Compt. rend. 1919, 168, 1253; 169, 162) have obtained compound of the type MI_3SO_3 , which they term sulphones.

SULPHONIC ACIDS $R \cdot SO_3H$. These acids may be conveniently described under two headings: (a) aliphatic sulphonic acids, (b) aromatic sulphonic acids.

Aliphatic sulphonic acids. These acids are not of much importance.

General methods of preparation.—(i.) By the oxidation of mercaptans, alkyl disulphides, or alkyl thiocyanates with nitric acid.

(ii.) Their salts and esters are formed by the interaction of alkyl iodides with alkali sulphite and silver sulphite and the required alcohol respectively.

(iii.) By the oxidation of sulphinic acids.

Properties.—They are mostly viscous liquids, readily soluble in water, and usually can be obtained crystalline. On heating they undergo decomposition; by fusion with caustic alkalis they are decomposed into alcohols and alkali sulphites, but they remain unchanged when boiled with aqueous alkali hydroxides. Phosphorus pentachloride converts them into sulphonic chlorides.

Aromatic sulphonic acids. These acids are easily obtained by digesting the substance to be sulphonated with sulphuric acid. The number of hydrogen atoms replaced depends on the strength of the acid and on the temperature. A small quantity of iodine added to the mixture is said to facilitate the sulphonation (Eng. Pat. 12260 of 1915). The course of the reaction is frequently modified by the presence and nature of a catalyst. Thus the presence of a little mercuric sulphate induces the formation of a mixture of the 1:5 and 1:8 anthraquinone disulphonic acids, whereas in the absence of mercury the product is a mixture of 2:6 and 2:7 disulphonic acids (D. R. PP. 149801 and 157123). The sulphonation of benzoic acid is likewise modified by the presence of mercury (Ber. 1907, 40, 2413). These acids are important as the source of many dyes; many dyes which are insoluble in water are converted into their sulphonic acids which are readily soluble. The aromatic sulphonic acids are also manufactured to be converted into phenols by fusion with caustic alkali. Many are also valuable as synthetic drugs (*q.v.*).

General methods of preparation.—(i.) By digesting the substance with sulphuric or anhydrosulphuric acid; or with chlorosulphonic acid when the sulphonic chloride is produced.

(ii.) By the oxidation of thiophenols or of sulphinic acids.

(iii.) By heating diazoamino compounds with sulphurous acid.

Of these methods the first is the most important. It is often somewhat difficult to isolate the acids, as they are readily soluble in water, are non-volatile, cannot be extracted from aqueous solutions with organic solvents or separated from other substances by steam distillation. The following method is usually employed: excess of sulphuric acid is removed from the sulphonation product by boiling with excess of barium carbonate; the precipitated barium sulphate is filtered off, and to the filtrate

which contains the barium salt of the sulphonic acid, sulphuric acid is added until precipitation no longer occurs. After filtering, the solution is evaporated to dryness when the acid is obtained either crystalline or as a syrup. Calcium carbonate may be used instead of barium carbonate, in which case, as the acid will contain a little calcium sulphate, alcohol is added to the final product, the calcium sulphate filtered off, and the alcohol removed by evaporation. Sometimes lead carbonate is employed, when the lead salt of the sulphonic acid is decomposed with hydrogen sulphide. These methods only apply when the barium, calcium, or lead salts are soluble in water (*cf.* Dennis, U.S. Pats. 1211923, 1212612, 1227252, 1229593, 1228414; Sachs and Byron, *ibid.* 1207798).

When two or more sulphonic acids are present, separation is usually effected by fractional crystallisation of their salts. If this is not effectual, they are converted into sulphonic chlorides by means of phosphorus pentachloride. The sulphonic chlorides are well-defined crystalline substances, which can easily be obtained in a pure state.

Benzene sulphonic acid may be prepared from bromobenzene, sodium sulphite, and copper sulphate in presence of water at 180° , and subsequently at 200° . Similarly, *p*-bromotoluene gives toluene *p*-sulphonic acid. Sodium *o*-bromobenzoate and sodium sulphite yield *o*-sulphobenzoic acid at 120° – 130° , or when boiled under reflux.

Properties.—The aromatic sulphonic acids are usually very soluble in water, and when obtained crystalline are often very hygroscopic. They can be salted out from aqueous solutions as sodium salts by the addition of sodium chloride. They gradually decompose when heated, so seldom have a definite melting-point. They are strongly acid substances, decomposing carbonates and dissolving certain metals with evolution of hydrogen. Benzene sulphonic acid is slowly attacked by 10 p.c. sodium hydroxide at 320° , but the naphthalene sulphonic acids readily yield pure naphthols. Benzene disulphonic acid is hydrolysed to phenol *m*-sulphonic acid; *o*- and *p*-phenolsulphonic acids give free phenol (Willson and Meyer, Ber. 1914, 47, 3160). Sodium benzene sulphonate fused with sodium hydroxide in absence of air at 300° – 350° gives a theoretical yield of phenol. The following are the principal reactions in which they take part:—

(i.) Phosphorus pentachloride or oxychloride converts their alkali salts into *sulphonic chlorides*.

(ii.) Fusion with caustic alkalis yields *phenols*.

(iii.) Distillation with potassium cyanide yields *nitriles*.

(iv.) *Hydrocarbons*, together with *phenyl sulphones*, are formed by distillation of the acids alone or with hydrochloric acid.

(v.) The sulphonic group may be replaced by the *nitro group* by the action of nitric acid.

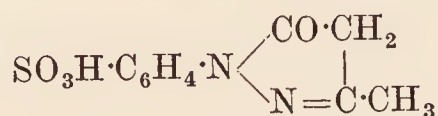
(vi.) The sulphonic group may be replaced by the *amino group* by the action of sodamide.

(vii.) The sulphonic chlorides are converted into *thiophenols* on reduction.

Anhydrides are obtained by the action of thionyl chloride on aromatic sulphonic acids. They are colourless or pale yellow crystalline

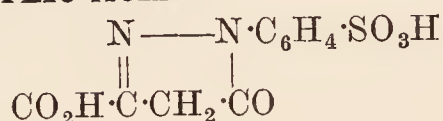
solids, stable towards water and weak alkalis. They react with alcohol, ammonia, and amines, producing the corresponding esters and amides, and can be sulphonated and nitrated. A number of them have been described by Meyer and Schlegl (Monatsh. 1913, 34, 561).

1-*p*-SULPHOPHENYL-3-METHYL-5-PYRAZOLONE



may be obtained by heating phenylmethylpyrazolone with fuming sulphuric acid and pouring the product into water; or by condensing phenylhydrazine *p*-sulphonic acid with ethyl aceto-acetate (Farbwerke vorm. Meister, Lucius und Brüning, D. R. P. 176954). Crystallises with 1 mol. H_2O . Sparingly soluble in water (*v. PYRAZOLONE*).

1-*p*-SULPHOPHENYL-5-PYRAZOLONE-3-CARBOXYLIC ACID



Formed by the action of ethyl oxalate on phenylhydrazine-*p*-sulphonic acid in presence of sodium acetate at 50° . When mixed with dilute hydrochloric acid, the acid sodium salt separates out. Used in making Flavazine.

SULPHOXYLATE-SALVARSAN. A substitute for novarsenobenzol or neo-salvarsan.

SULPHUR. Sym. S. At. wt. 32.065 (Richards and Hoover). According to Aston, sulphur has atoms or isotopes whose mass is twice the atomic number. This substance has been known from the earliest times. Its ancient and familiar name of brimstone (A.S. *byrnan*, to burn, and *stane*, a stone, probably corrupted from *brinstone* or *brenstone*, *i.e.* fiery stone) is based upon the circumstance that it is combustible and that, when ignited, it will continue to burn in presence of air with a characteristic blue flame until it is entirely consumed. To the alchemists the term sulphur was practically synonymous with the principle of inflammability, and hence was not necessarily restricted, as now, to the element.

Sulphur occurs in the free state in the neighbourhood of volcanoes, active and extinct, and is a characteristic product of volcanic action. Volcanic sulphur is found largely in Italy, Sicily, Iceland, Mexico, North and South America, Aleutian Islands, Japan, Asia, New Zealand, and other parts of the world, and some of these places constitute valuable sources of supply. Vanua Lava, an island in the Banks Group of the New Hebrides, consists of a mountain 1600 ft. high composed of sulphur of 99 p.c. purity.

Deposits of free sulphur occur in sedimentary rocks as a product of bacterial action, certain bacteria having the property of reducing sulphates and of assimilating sulphur to a relatively large extent. It may also have been formed by the reducing action of hydrocarbons on gypsum. In union with a great variety of metals sulphur occurs as *sulphides*, and some of these compounds constitute important metalliferous ores. Combined with oxygen and bases, sulphur is found in nature as *gypsum*, *selenite* and *anhydrite* (calcium sulphate); as *heavy spar* (barium sulphate); as *celestine* (strontium sulphate);

as *Epsom salts* and *kieserite* (magnesium sulphate), etc.

Sulphur is also found in nature combined with hydrogen, as *hydrogen sulphide* or *sulphuretted hydrogen*, and occasionally with carbon and oxygen as *carbon oxysulphide* in a number of mineral waters which are supposed to owe their therapeutic value to such sulphur compounds.

Sulphur is found unoxidised, but combined, in vegetable and animal tissues, in a variety of proteid substances; in the hair, nails and horn; in the taurin of the bile, in the cystine in urine, &c. Many volatile oils, *e.g.* oil of mustard, oil of garlic, &c., are composed of organic sulphur compounds to which their characteristic smell and other properties are due.

For many years past, and until the year 1903, about 95 p.c. of the world's supply of sulphur was mined and prepared for use in Sicily, the greater portion of the remainder being obtained from the Romagna in Italy, and from Japan. But the successful application of the Frasch process, a description of which follows, to the winning of pure sulphur at a low cost from deposits at Calcasieu Parish in Louisiana, U.S.A., long known but unworkable by ordinary mining methods, resulted in a reduction at the end of 1912 of sales of Sicilian sulphur from the 95 p.c. per annum of the world's consumption above mentioned to about 50 p.c.

In the year 1900 the production in the United States was about 2000 tons. After the Frasch process was developed upon a practical scale during the year 1902 the production increased to 30,000 tons; in 1903, to 137,292 tons; and the production in 1913 is upwards of 300,000 tons per annum. Four States—Louisiana, Nevada, Utah, and Wyoming—produced practically all the sulphur. All the requirements of the United States are met by Frasch sulphur with the exception of Japanese sulphur supplied to the western coast, and the imports from Sicily have fallen until they may now be regarded as negligible. The exports from the United States of Frasch sulphur have thus far not been developed to any great extent, but since 1905 about 30,000 tons have been sent annually from Louisiana to France. Having regard to the stocks accumulated, to the vast tonnage of obtainable sulphur stated to be in sight, and to the extremely low cost of winning sulphur of great purity as compared with the methods employed in Sicily, it would appear that should it be considered desirable to extend the export trade of Frasch sulphur there is no reason why it should not be done upon a very large scale.

The Frasch process has proved to be applicable to the extraction of sulphur from the deposits in the dome formations of the Gulf Coastal-Plain regions, of which the deposits at Calcasieu in Louisiana constitute a portion. Other deposits have been located in this formation, and one in Texas at Bryan Hill, about forty miles from Galveston, is worked by the Freeport Sulphur Company, by a modification of the Frasch process. The Texas Gulf Sulphur Company produces 1200 tons a day, most of which is shipped from Texas city. Other large deposits have been found at Hoskins Mound, Texas.

Sulphur deposits in other parts of the world

are now well known, and in addition to those already named may be mentioned those in the Caucasus, in Jebels Kabrit and Jemsah in Upper Egypt, and on White Island in New Zealand.

Deposits of sulphur of the solfatara type occur in many of the Aleutian Islands; one deposit is located in the crater of Makushin Volcano on Unalaska Island, where it is estimated that from 10,000 to 15,000 tons of sulphur can be mined. Another deposit, covering from 15 to 20 acres and containing about 1200 tons per acre, occurs on Akun Island, while a third deposit is found at Stepovak Bay.

Japanese sulphur is of high purity and has a market to the extent of about 30,000 tons per annum. Of the total output, about 90 p.c. is obtained from the deposits which have been worked for many years in the volcanic district of Central Hokkaido. It is mainly shipped to the Pacific ports of the United States and to Australia. The sulphur is of what is known as the solfatara type and is deposited in cracks in the lava and in the tuffs owing to the interaction of sulphuretted hydrogen and sulphurous acid gases which have their origin in active or expiring volcanoes.

Italian sulphur.—Between 30,000 and 40,000 tons of sulphur are obtained per annum from deposits in the Romagna which have long been worked. The sulphur thus obtained is almost exclusively employed in Italy for agricultural and viticultural purposes.

Sicilian sulphur is stated to have been employed in industry during the past 300 years. It is estimated that about 16,000,000 tons have been mined and extracted up to date, and until the introduction of Louisiana sulphur, extracted by the Frasch process, Sicily controlled the sulphur industry of the world.

The sulphur occurs in Miocene strata and constitutes what is known as the 'gypsum' type as distinct from the 'solfatara' type. Marls, shale and gypsum are prominent constituents of the sedimentary rocks in which the sulphur is produced. The reducing action of the bituminous matter under efficient conditions of temperature and pressure upon gypsum results in the formation of calcium sulphide, which in turn is acted upon by oxygen, carbonic acid and moisture, producing calcium carbonate, sulphuretted hydrogen and polysulphide of lime. The latter in turn yields calcium carbonate, sulphur and sulphuretted hydrogen. It is stated by Fuchs and De Launay (*Traité des Gîtes Minéraux*, p. 274) that 24 p.c. of sulphur would represent about the average that would be deposited as the result of these reactions, and inasmuch as this percentage may be taken as representing the average amount of crude sulphur found in Sicilian sulphur rock, it is regarded as a strong argument in favour of the sulphur being deposited in the manner suggested.

The mines are distributed throughout the provinces of Caltanissetta and Girgenti. They cover an area of about 100 miles by about 55 miles. The deposits of sulphur (*sofàre*) vary in depth from 150 ft. to about 650 ft., and in the deep mines the ore is now all brought to the surface by mechanical means: in the past it was practically all dealt with by manual labour.

The ore varies very considerably in its total sulphur content. The rich ore contains from 30 p.c. to 40 p.c. of crude sulphur, which, depending upon the method of extraction employed, yields from 20 p.c. to 25 p.c. of commercial sulphur. But the average ordinary ore contains from 20 p.c. to 25 p.c. and yields from 10 p.c. to 15 p.c. of commercial sulphur. In some ores the sulphur is as low as 8 p.c., but unless they contain about 15 p.c. they do not pay for working by the method adopted in Sicily.

In addition to the 16,000,000 tons which have been stated to have been mined, prepared and sold, it has been officially reported that the quantity of commercial sulphur still in sight in the Sicilian deposits amounts to about 34,000,000 tons.

The effect of the Louisiana sulphur competition upon Sicilian production may be illustrated by the fact that in 1903 there were 757 active sulphur mines in Sicily and that nearly 40,000 operatives were employed. To-day the number of mines worked is about 400 and the number of operatives about 20,000.

It must be admitted that the methods of extracting sulphur in Sicily were not adapted to meet serious competition, although substantial progress has been made since the regenerative furnace has been employed. Since 1850 the method mainly employed was to submit the ore containing not less than 15 p.c. of sulphur to combustion, the necessary fuel being mainly provided by the sulphur itself, about one-quarter of which was thus consumed. In this process the ore is massed in circular heaps of about 60 ft. diameter and about 9 ft. deep. The heaps are coated with moistened ash obtained from the burnt ore. Each heap is provided internally with a sloping floor fitted with compartments in which the fused sulphur collects and from which it is subsequently recovered in the form of loaves weighing about one hundredweight each. The heaps thus prepared are known as *calcaroni*. The process is started by setting fire to wood fuel from the top of the heap and the heat is maintained by means of lighted wood. The loss of sulphur by combustion is so considerable that the yield of sulphur obtainable as loaves is only about 60 p.c. of the total sulphur contained in the ore. In addition, the pollution of the atmosphere is very great, and where the *calcaroni* system has been worked upon a continuous scale, much damage is caused to trees and plants in the surrounding country.

In 1880 Robert Gill introduced his regenerative furnace into Sicily, and it has since been improved and developed very considerably. The object of its construction was to effect the easy regulation of the combustion and to provide a continuous process. In order to effect this, two large square brick furnace chambers, provided with double floors on which the molten sulphur collects and subsequently cools and solidifies, are independently connected with a chimney stack, and the heating of the chambers is so regulated that when the ore has been treated in one chamber the heating of the other chamber is at once started, and thus the process becomes continuous. Still greater improvements have been effected by the provision of as many as six large circular chambers connected with the

chimney instead of the two square chambers above-mentioned, and these have been still further improved by air-regulating devices which are found in the Sanfilippo furnaces now mainly employed in Sicily. By this method about 80 p.c. of sulphur can be extracted, a great advance upon the yield obtainable from the *calcaroni*, which have now been practically superseded.

Attempts have also been made in Sicily to extract sulphur by means of superheated steam under pressure, and in this way it has been found possible to obtain a yield of sulphur as high as 90 p.c. of that present in the ore. But steam extraction, although successfully applied in Romagna, would not appear to be practicable upon a large scale in Sicily owing to the cost of fuel and the losses occasioned when much gypsum is present, as is often the case.

It is difficult to arrive at accurate figures as regards the present cost of sulphur production in Sicily, but it would appear that the position may be fairly summed up by stating it at 40s. per long ton, and this is probably placing the figure too low. This price of Sicilian sulphur production must undoubtedly be taken into consideration when making a comparison between the future industrial possibilities of Sicilian sulphur and those of other deposits which have been referred to.

Crude Sicilian sulphur, which constitutes a large proportion of the island sulphur trade, contains impurity ranging in amount from about 2 p.c. to about 11 p.c. It is known as *Greggio*, and its price varies according to the amount of impurity. Thus it is graded as 'Best Unmixed Seconds,' 'Best Unmixed Thirds,' and 'Current Thirds.' These three qualities practically represent the entire Sicilian brimstone trade. The difference in price between the best and worst qualities is about 5s. per ton, and if pure sulphur be required it is prepared by refining and as a result the impurity of the commercial refined product is reduced to about one-half p.c. It is then sold as *Raffinate*.

In its preparation the crude sulphur is subjected to sublimation and one of two different kinds of product may be prepared. If the temperature of the condensing chamber is kept well above 100°C. then the molten sulphur is allowed to flow into moulds and when solidified is sold as refined sulphur. If the temperature is kept below 100°C. flowers of sulphur are formed, for which there is a very considerable demand. When sulphur is used for application to vines, the crude sulphur is ground so as to pass through fine-mesh sieves, or it may be winnowed by means of compressed air. When thus treated the sulphur is found to adhere to the foliage of the vine, whereas if sublimed and condensed it will not satisfactorily adhere.

The history of the Sicilian sulphur industry is characterised by the remarkable changes to which it has been subjected. Previous to the year 1838, sulphuric acid, wherever manufactured, was made from brimstone, and the supply came practically from Sicily only. The alkali industry was, to a great extent, dependent upon the price charged for brimstone and the fixing of that price was in the hands of those who controlled the Sicilian industry. Accordingly, attempts were made to employ pyrites as the

source of sulphur instead of brimstone, and in 1813 a patent was granted to Hill, of Deptford, in connection with this application. But Sicily continued to hold the sulphuric acid raw material trade until the year 1838, when a monopoly was granted by the King of Naples for the export of Sicilian sulphur to M. M. Taix & Cie., of Marseilles. The result was to raise the price of brimstone from £5 to about £14 per ton. The immediate answer of Great Britain was that many patents were taken out in connection with the application of pyrites to the manufacture of sulphuric acid, and a large plant was successfully installed by Thomas Farmer of London. As a result, brimstone was speedily replaced by pyrites, and Sicily lost nearly the whole of this trade. A certain proportion of the world's supply of sulphuric acid is, however, still made from brimstone, owing to the fact that brimstone-made acid is free from arsenic, and as such is suitable for the preparation of sulphuric acid used in the preparation of products connected with food and pharmacy. Notwithstanding that the arsenic can be effectually removed from sulphuric acid made from pyrites, brimstone is still frequently employed in this connection.

In order to meet the competition occasioned by the application of the Frasch process to the winning of sulphur in Louisiana, Professor G. Oddo proposed the utilisation of 'smalls' (*sterro*), which constitute about 20 p.c. of the Sicilian sulphur ore, for the production of sulphuric acid by means of the Herreshoff furnace. A large-scale plant was erected and worked, and it is claimed that successful results were achieved. Owing, however, to the very small percentage of sulphur contained in the 'smalls,' as compared with that contained in pyrites employed in industry, it was found that the cost of carriage would render the export of *sterri* to other countries impossible, and that the only chance of success was to start a sulphuric acid industry upon a very large scale in Sicily. This, however, has not yet been attempted.

The industry was not only damaged as regards the sulphuric acid industry by the rise in price of sulphur to £14 per ton as above-mentioned, but as might have been expected, great harm was done in other directions. As a result, the monopoly was withdrawn and the price of £5 per ton re-established. Excepting the use of sulphur in the manufacture of sulphuric acid, all went smoothly as regards the world's supply until the Chance-Claus process for the recovery of sulphur from alkali waste became a success. From about 1891 to 1896, it was believed that this process could not only be applied to the waste then being produced in the alkali industry, but also to the recovery of sulphur from the tip heaps which had been accumulating for many years past. Advantage was taken of the possibility to cause internal competition amongst the producers in Sicily, with the result that the market was completely disorganised and wages were reduced almost to starvation rates. This depression of prices reacted in turn upon the price of the Chance-Claus sulphur produced in England. When it was ascertained that it was not possible to extract the sulphur from the tip heaps waste,

owing to the change it had undergone through oxidation, and that the amount produced from fresh waste would not exceed 50,000 tons per annum, and therefore could not affect the Sicilian market, the price was fixed by speculators at about £5 10s. per ton. This action was resented by the consumers, who took the necessary steps to start a keen fight, not only between the producers in Sicily but also in Great Britain, with the result that the selling price of brimstone was reduced to 45s. per ton, out of which had to be paid the export tax of 8s. per ton. This state of affairs continued for some time, until 1896, when Sicily was on the verge of revolution as well as ruin.

It was then that efforts, initiated in England, were made to combine the Sicilian and British interests and to regulate the trade of the world, so that the price could no longer be dictated by speculators. At the same time, steps were taken to remedy the serious grievances of the Sicilian workmen and owners of mines. The movement, which resulted in the formation of the Anglo-Sicilian Sulphur Company, was heartily supported by the Italian Government and notably by the Marquis di Rudini, then Prime Minister in Italy, with the result that the capital for the organisation of the business having been obtained mainly in England, a Royal Decree was then issued, and subsequently confirmed by a special Act of Parliament by which the heavy export tax was abolished, wages of the workmen increased, child labour, previously employed to a very large extent, was abolished, income tax and other heavy charges were withdrawn, and a tax of one lire per ton on sulphur exported was substituted. The bulk of the stock both in Sicily and England was taken over at an agreed and reasonable price, and an agreement was made whereby about 65s. per ton would be paid to the producer in Sicily, and the production regulated so as to keep in touch with the quantity exported. The capital of the company was one million sterling, of which £735,000 was fully subscribed.

The formation of this company resulted in the maintenance of fair and satisfactory prices for sulphur, and of peace and prosperity for Sicily for a period of about ten years. Both buyers and sellers were satisfied with the conditions under which the company's business was carried on, and the variations of selling price during the ten years did not amount to more than 5s. per ton.

The contracts which the company made with the producers, and the stock of sulphur which it acquired when it was formed, gave it a control over about 75 p.c. of the total production of Sicily, and this led to the complete control of the market. The company also had the right, under its contracts, to call for a reduction of 18 p.c. of the output in any year in which the output should exceed the sale. But the producers were also entitled to be paid 1 p.c. extra for each 3 p.c. reduction in the price of sale. The company was only interested in the sale of sulphur and was in no way financially interested in the mining or in the process of production. It may be stated that the operations of the company were quite successful to all interested, and it would undoubtedly have continued to exist, and to prosper, but for the unexpected competition

caused by the successful development of the Frasch process. It succeeded in obtaining a fair but not excessive market price for sulphur all over the world. For instance, in May, 1896, just previous to the formation of the company, the price of 'seconds' in New York was about 63s. per ton. In October of the same year, after the company had started operations, the selling price of the same quality was 104s. per ton.

The stock acquired by the company was about 60,000 tons, which, as representing about 70 p.c. of the industry of Sicily, was to be regarded as quite a satisfactory quantity. During the first eight years of the company's existence, no complications of any kind were experienced, but during the year 1904, the Frasch process was proved to be an industrial success, and the United States sulphur sales were from that time gradually taken away from the Anglo-Sicilian Sulphur Company. As a result, the company in July, 1906, exercised its option of terminating its agreement with the producers and was in due course liquidated with satisfactory results to the shareholders. The effect of competition with Louisiana sulphur will be appreciated when it is stated that the stock of the Anglo-Sicilian Sulphur Company, when it terminated its contracts, amounted to 360,000 tons, and at the end of June, 1912, the stock of sulphur in Sicily amounted to no less than 546,902 tons. This had been reduced by the end of January, 1913, by limiting production, to 441,775 tons.

The Italian Government found it necessary again to support the sulphur industry when the Anglo-Sicilian Company was about to be liquidated, and with its assistance the stock of the company was purchased at 49s. 2d. per ton, and was paid in Government debentures yielding 3·65 p.c. interest per annum redeemable in twelve years. The industry was placed, as from the 1st August, 1905, under the direction of the 'Consorzio obbligatorio per l'Industria Solifera Siciliana,' which was charged with the sale and regulation of the production of Sicilian sulphur for a period of twelve years. The Consorzio was assisted by the Government so as to be provided with sufficient capital to permit of its paying four-fifths of the selling value in advance to the producer for delivered crude sulphur, and also had full power to limit production. Sulphur was exempted from all taxation.

Considering the difficulties that have had to be faced as a result of the competition with Frasch sulphur, it may be stated that the Consorzio has been a successful organisation. Some modifications of the law relating to it were passed in Parliament in the years 1907, 1908, and 1909, by means of which the number of directors was reduced and full powers were given to restrict the output from the mines to the quantity sold for export.

Italian sulphur production in 1922 fell to 172,000 metric tons, as compared with 274,000 tons in 1921 and 385,000 tons in 1913; exports, however, increased considerably as compared with 1921, a year of intense crisis in the sulphur trade of Sicily, states the International Year Book of Agricultural Statistics, 1922, published by the International Institute of Agriculture (Rome) and quoted in the Board of Trade Journal. The United States, in 1922, maintained its sulphur output (1,860,000 metric tons)

at almost the highest level, which was attained in 1921, and exceeded the 1913 yield of about 1350 metric tons. The exports from the United States in 1922 amounted to 496,000 metric tons, a figure never previously reached. Regarding the countries which notably increased their imports of sulphur during 1922, both as compared with 1921 and with 1913, Germany, France, the United Kingdom, Sweden, and Canada may be mentioned. Prices of sulphur, both in Italy and in the United States, were in 1922 fixed at a much lower level than in 1921. In the United States the monthly quotations were even below those obtaining before the war.

Louisiana sulphur.—The deposits from which this sulphur is obtained are geologically associated with 'Dome Formations,' which constitute a striking feature of the coastal plains which extend through the States of Louisiana and Texas and the Gulf States of Mexico. Petroleum and rock salt of remarkable purity (98–99 p.c.) are also found in these formations in abundant quantity. The oil was first exploited, and it was when oil drilling was being carried out by the Louisiana Oil Company, in the year 1865, at the head of Bayou Choupique, about fifteen miles west of Lake Charles, that the first sulphur bed was found at a depth of 443 ft. It was proved that this sulphur bed had a depth of about 100 ft. Further detailed examination showed that the sulphur deposits have an average overburden of about 464 ft., consisting of about 376 ft. of clay and sands (pleistocene), quicksand and gravels (Port Hudson and Orange sand groups), and about 88 ft. of soft rock, mainly grey limestone. The average depth of the sulphur bed is 125 ft. Beneath the sulphur is gypsum with occasional layers of sulphur.

Between the years 1868 and 1895 many attempts were made to win the sulphur by ordinary shaft mining and by modifications of the same. They all resulted in failure, loss of many lives and great loss of capital. Among the companies formed for the purpose of mining the sulphur may be mentioned the Calcasieu Sulphur and Mining Company, the Louisiana Sulphur Mining Company, the American Sulphur Company, a French company which spent £300,000 upon a scheme for the employment of machinery specially devised for overcoming the difficulties, and an Austrian company. These difficulties were mainly twofold: to resist the lateral pressure upon the shaft due to the enormous amount of moving water contained in the quicksands, and to prevent the inrush of the sand waters into the sulphur bed, when it had been penetrated, owing to the fact that there was no roof over the sulphur bed. These waters were found to be saturated with sulphuretted hydrogen and sulphurous acid gas which proved fatal to the miners. In 1893, E. P. Rothwell, acting as manager to a New York company, sought to overcome the difficulty by lining the shaft with two cast-iron tubes cemented together. The lateral pressure was thus withstood and the sulphur bed was reached, but the inrush of gases again proved fatal to the workmen and the scheme had to be abandoned.

It will be seen that during no less than thirty years, successive attempts were made to win sulphur from what were proved by borings

to be vast deposits, but ordinary mining operations were found to be absolutely impracticable.

The Frasch process.—This may fairly be described as one of the triumphs of modern technology, and the result of its successful development has been to provide a great industry for the United States, which it did not previously possess, and to remove from Sicily to that country the domination of the conditions regulating the world's supply of sulphur.

Herman Frasch, who had long been engaged in industrial research work in the United States in connection with petroleum drilling and refining, heard in 1891 of the difficulties connected with the mining of Louisiana sulphur, as above described. As a result of a study of the local conditions he arrived at the conclusion that the problem might be solved provided he could introduce superheated water into the sulphur bed through a tube passing through the quicksands at a temperature at or above the melting-point of sulphur and then raise the molten sulphur through another tube to the surface. The molten sulphur would then solidify on cooling at the surface, and the sulphur thus obtained would necessarily be of high purity. To succeed with this scheme meant not only to overcome the difficulties in connection with lateral pressure upon the tubes already alluded to, not only to introduce the superheated water to the sulphur about 500 ft. below the surface at the required temperature, but, recognising that a pool or well of melted sulphur would be formed below the bottom of the tube by this superheated water, it would be necessary to raise this molten sulphur from the pool or well to the surface before it could be cooled below melting-point by the incoming water from the quicksands.

He and his associates purchased land within a short distance of the sulphur mine then being worked by the New York Company. He drilled four wells to a depth of 2000 ft. each and found no sulphur. He concluded that the New York company's property was located where the sulphur was concentrated in bulk, and in conjunction with his associates he acquired this property in the name of the Union Sulphur Company of Cleveland, Ohio. It consisted of a flat-lying area of 5000 acres, situated near the parish of Calcasieu, Louisiana, 80 miles from Port Arthur, Texas, on the Gulf of Mexico, and 228 miles from New Orleans. The property is about 50 miles east of the great Texas oil-field at Beaumont and is geologically the eastern extension of that field. As a result of many trial drills it is estimated that the Louisiana deposits contain not less than 40 million tons of sulphur, and that it would be a conservative estimate to conclude that not less than half this quantity could be brought to the surface by the Frasch process.

As may be imagined, many difficulties were encountered in working out the process, and it was not until the year 1903, when 35,000 tons of sulphur were brought to the surface, that success may be said to have been achieved. The chief trouble arose in connection with the pumping up of the molten sulphur, mainly due to the breaking down of the valves owing to corrosion. Zinc and aluminium valves were respectively tried, but were found incapable of

standing the strain. Ultimately, pumping was replaced by an 'air lift,' by means of which the molten sulphur is forced through a tube to the surface. An additional advantage resulting from the use of the compressed air is that the specific gravity of the mixture of air and sulphur which is raised is lower than that of molten sulphur by itself, and hence the strain upon the great length of piping is reduced. The mixture employed is two parts by volume of air to one part of molten sulphur.

The following may be regarded as a substantial description of the process as worked: A well, 17 ins. in diameter, is bored to a depth of some 50 ft. This is not provided with a casing, but a mixture of clay and water is pumped down with a view to fill up the interstices in the sand, whereby caving is greatly reduced. Within this well a wrought-iron pipe, 13 ins. in diameter, is sunk to a variable depth, dependent upon outside pressure, and sometimes it can be arranged to reach the bottom of the quicksands at about 250 ft. A mixture of clay and water is also employed in connection with this pipe, and in addition to helping to support the walls it materially facilitates the withdrawal of the pipe when the well is exhausted, thereby effecting a considerable economy in the working of the process.

Inside this 13-inch diameter pipe, an 8-inch diameter pipe is driven to the bottom of the sulphur bed. Water and clay are also used. Those sections of this pipe which are intended to be in the sulphur bed are perforated with holes of half an inch diameter, arranged in spiral form, the holes being six inches apart. This arrangement has for its object to prevent gypsum, &c., getting to the bottom of the pipe. The superheated water, which is conveyed through this pipe to the sulphur bed, has free access to the sulphur throughout the entire thickness of the deposit, and any substance which should by chance get into the bottom of the pipe causes no trouble. Inside the 8-inch diameter pipe, an unperforated 6-inch diameter pipe is sunk to the bottom of the sulphur bed. Superheated water is also pumped down this pipe. Enclosed in this 6-inch pipe is an unperforated 3-inch diameter pipe, through which the molten sulphur is raised to the surface. Inside this 3-inch pipe is driven to the bottom of the bed a 1-inch diameter unperforated pipe through which the compressed air is forced.

Superheated water is pumped down the 8-inch and 6-inch pipes. The water from the 8-inch pipe melts the sulphur which (sp.gr. 2.06) sinks down alongside the pipe to the bottom of the sulphur bed. The water in the 6-inch pipe mainly serves to keep the sulphur hot in the enclosed 3-inch pipe, thereby preventing solidification on its way to the surface. Compressed air, at a pressure of 250 lbs. per square inch, is forced down the 1-inch pipe to raise the sulphur by the 'air lift.' This pressure is found sufficient in practice to raise the sulphur to the surface, as the air is helped by the head of water in the 6-inch and 8-inch pipes to overcome the weight of sulphur in the 3-inch pipe.

One of the most important features of the process—indeed, that upon which successful working mainly depends—is the maintenance of a proper adjustment between the pressure

of the superheated water and the air pressure so as to allow of the uninterrupted flow of sulphur through the 3-inch pipe. If the air pressure be too great, the liquid sulphur is kept away from the 3-inch pipe and superheated water gains entrance to it. When the water and the molten sulphur come into contact, the sulphur granulates, subsequently causing clogging in its upward path. As a result there is irregular discharge of the sulphur, and this means such great local pressure in the pipe that serious breakage is apt to occur. It has been found advisable, in this connection, to so adjust the respective lengths of the pipes that the 8-inch and 6-inch pipes are a few inches shorter than the 3-inch and 1-inch pipes as they stand in the well. What is aimed at is to have a constant pool of liquid sulphur surrounding the bottom of the 3-inch pipe.

It has been found advisable to introduce sawdust with the superheated water once the pool of liquid sulphur has been formed. It is found that this prevents to a very great extent the flow of quicksand water into the pool with consequent lowering of temperature. When the well is exhausted, before the withdrawal of the 8-inch pipe, it is now usual to replace with earth the space of the extracted sulphur and thus prevent subsequent subsidence of the earth as much as possible. In order to obtain the sandy earth necessary for this purpose, the Union Sulphur Company have provided a dredging plant in the vicinity of their works with a capacity of 4000 cubic yards per day. Notwithstanding this precaution, considerable subsidence is stated to have taken place.

It is obvious that in working this process so as to produce a yield of, say, 250,000 tons of sulphur per annum, an enormous supply of water is necessary. It is stated that the average daily consumption is about 7,000,000 gallons. To provide for this, the Union Sulphur Company have constructed a pumping station on a river about six miles from the works, to which the water is conveyed by means of a canal; as a standby there is also provided at the works a reservoir covering 150 acres.

To supply the necessary heat and power, the latter constituting only a fractional percentage, it is found that each well requires a battery of 15 or 20 boilers of 50 h.p. each. Steam pressure runs at about 100 lbs. The total boiler capacity at present installed is stated to be about 25,000 h.p. Crude oil is used as fuel and its local availability and cheapness have undoubtedly largely contributed to the successful working of the Frasch process. There are two oil burners to each boiler. It is stated that the present daily consumption of crude oil is about 700 barrels at each battery, and that the average annual consumption is upwards of 1,000,000 barrels.

The boilers supply steam to six heaters, each 15 ft. high and 3 ft. in diameter. Two direct-acting horizontal pumps, working under a stroke of 38 to 40 per minute, supply each heater with the necessary water at a temperature of 140°F. (C.=60°). The steam enters the heaters at the top and the water at the bottom, and the superheated water leaves the heater at a temperature varying from 340°F. (C.=171.1°) to 360°F. (C.=182.2°) under an

absolute pressure of 104 lbs. to 140 lbs. The water is conducted to the well by means of insulated pipes. The melting-point of sulphur is 239°F. (C.=115°), and at a temperature slightly below this it will granulate.

It has been estimated that of the total heat units employed, 0.5 p.c. only are utilised in melting the sulphur. The temperature of the quicksand water, of which there is a great influx to the sulphur bed during the operation of the process, is low and has to be raised before the sulphur can be melted. The well gives out when the cavity from which the sulphur has been extracted becomes too large to permit of the necessary temperature being maintained.

Each well is driven by the ordinary oil-well driller mounted on a derrick from 75 ft. to 100 ft. high; five men generally constitute the drill gang. The average time required for drilling the well may be said to be between three and four weeks. The speed of drilling naturally varies with the nature of the material to be passed through, but it is stated to average 80 ft. per day through the quicksand, from 5 ft. to 8 ft. per day through the limestone rock, and 20 ft. to 30 ft. per day through the sulphur.

The average cost of sinking each well, exclusive of pipes, is stated to be about £400, and the expense of working the well during its life, including oil, labour, depreciation, &c., will average about £2000 more. The wells are sunk in groups, and are placed from 50 to 100 ft. apart. The output from a well is obviously liable to considerable variation. It is stated that as much as 73,000 tons of sulphur were obtained from one well. This is undoubtedly exceptional, but a good idea of the output may be obtained from the statement that as much as between 400 tons and 500 tons have been produced per well per day during some months. The total annual production is restricted to meet the world's demand, in conjunction with other sources of supply, but the average is now not less than 250,030 tons per annum.

On reaching the surface the sulphur is conducted through a pipe supported on a light framework to a bin roughly constructed of beams in which it quickly solidifies. At the early stages of working these bins were divided into compartments into which the sulphur was allowed to flow until it had acquired a depth of 9 ins., when the flow was diverted to another compartment, so as to permit of the cooling of that collected. After solidification, another 9 ins. of sulphur was allowed to flow in, and the bin was by this method gradually filled up. The bins as now used are about 150 ft. by 250 ft. and about 65 ft. high. The sulphur is delivered into the centre of these bins and caused to spread in layers about 1 in. thick. By this method of working, the cooling is sufficiently rapid to permit of continuous operation. As much as 150,000 tons of sulphur have thus been accumulated in one series of bins.

From 600 to 700 men are employed in winning and despatching the sulphur, and, having regard to the quantity dealt with, this is a notable proof of the up-to-date character of the labour-saving methods adopted. A comparison of these figures with the labour employed for the Sicilian output is vastly in

favour of the Frasch process. Further, if the total cost of obtaining the sulphur be considered, it is obvious that commercial competition by Sicily with Louisiana would be impossible, but the supply of the world's consumption from the respective sulphur-producing countries is now said to be regulated by arrangement, so that Sicilian sulphur is able to realise a reasonable profit.

In order to remove the sulphur from the bins to the railway trucks, the wooden hoarding is removed and blasting applied to the bottom of the sulphur. In this way the sulphur on being shot down by the blasting is so broken up that it can be picked up by grab buckets, which, by means of cranes, discharge it into wagons at such a speed that a 35-ton wagon can be filled in about 14 minutes. It is stated that as much as 1000 tons per day have thus been loaded for periods of 20 to 30 consecutive days.

For some considerable time after the process was started, the sulphur was conveyed by rail to New Orleans, about 228 miles distant. This was superseded by the construction of a special line, 68 miles in length, to Port Sabine, Texas. The cost of transport to New York has, in this way, been reduced to about one-third of what it previously was. The loading on to ships at Sabine is effected by mechanical arrangements, thereby reducing the cost to one-tenth of what it used to be at New Orleans, and it is stated that the sulphur can be evenly loaded on to the ships at the rate of 600 to 800 tons per hour. The company owns ships specially constructed for sulphur transport, and one of them will carry 5500 tons.

The stocks of Louisiana sulphur in the United States, France, and Hamburg may be said to amount to fully 400,000 tons.

The sulphur obtained by the Frasch process is of a very high degree of purity, from 99.93 p.c. to 99.98 p.c., and in addition only contains a trace of water. The process is only applicable when the deposit is especially rich in sulphur—say, between 60 p.c. and 70 p.c.—and for this reason, amongst others, it is not available for use in Sicily.

Sulphur production in Australia.—The Commonwealth Government has decided to pay a bounty of £2 5s. a ton on all sulphur produced in Australia from local pyrites and other sulphide ores or concentrates. When sulphuric acid is produced from Australian pyrites and other sulphide ores or concentrates, the bounty will be paid on as much sulphur as would be necessary to produce it. The Commonwealth Parliament have passed a bill providing for the appropriation of £100,000 each year for the payment of their bounty, and another bill allowing the free importation of sulphur as long as the bounty is payable.

Several large companies have agreed to instal plants for the purpose, which will be sufficient to provide for all Australian requirements (Comm. Int. J. Canada, Oct. 20, 1923; J. Soc. Chem. Ind. 1923, 42, 1150).

RECOVERY OF SULPHUR FROM THE VAT WASTE.

The alkali waste was for many years a great nuisance, not only to the manufacturers, but to



LOUISIANA SULPHUR MINES.
Filling up a bin (a block) fifty feet high.



the neighbourhood of the factories producing it. The waste, under the influence of moisture and the oxygen and carbonic acid of the atmosphere, decomposed on the waste tips on which it was deposited, giving off a strong smell of sulphuretted hydrogen, and contaminating all drainage of surface water which passed through it. As is evident from the description of the Leblanc soda process, this waste contains the sulphur originally burnt in the pyrites, and formed into sulphuric acid, and which is then changed by decomposition with common salt into the sodium sulphate charged into the black-ash revolvers.

The obvious remedy for the nuisance as well as to avoid the loss of sulphur was to recover the sulphur from the waste, and for many years work was done and processes were invented to this end.

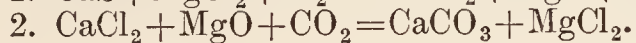
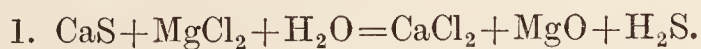
The recovery of sulphur, as such, from the calcium sulphide contained in alkali waste, a by-product of the Leblanc process, and the conversion of the calcium, with which it was previously combined, into an industrially available product, was taken in hand by several recognised leaders of the alkali industry. But it required about fifty years of almost continuous work before commercial success was achieved.

As the difficulty was finally solved by the Chance-Claus process, it will suffice to do little more than mention some of the principal processes previously invented and tried.

J. L. Bell in 1852, Ward 1862, Hewitt 1877, Kynaston 1885, Parnell and Simpson, Schaffner 1862, Mond 1862, Schaffner and Helbig 1878, proposed processes for this purpose.

The processes of Mond and Schaffner were both worked for some time on the large scale, and both depended on the partial oxidation of the CaS in the waste by the oxygen of the air which rendered a considerable proportion of the sulphur soluble in the form of CaS_2H_2 , CaS_2O_3 , and polysulphides. The solution so obtained on addition of hydrochloric acid deposited sulphur.

The Schaffner and Helbig process depended on the power of MgCl_2 to decompose CaS at the boiling-point, and the process was expressed by the following equations:—



An account of this process is given by Chance in *J. Soc. Chem. Ind.* 1882, 266.

Other processes were those of Kraushaar, *Dingl. poly. J.* 226, 412, and Alkali Inspectors' Report, 1877–1878, 15 and 35; Opl's process, *D. R. P.* 23142; Miller and Opl process, *Eng. Pat.* 2334, 1884. The last-mentioned process was tried at the Rhenania Chemical Works (*see* Hasenclever, *Chem. Ind.* 1889, 434).

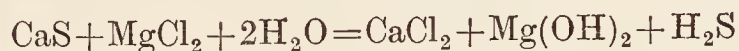
In 1837 Gossage devised a process at the development of which he worked for many years. It was based upon the decomposition of the calcium sulphide by means of carbon dioxide obtained from lime-kiln working, and the subsequent recovery of the sulphur from the sulphuretted hydrogen gas thereby generated. But although his labours undoubtedly contributed largely to the ultimate solution of the problem, he was unable himself economically to produce either sulphur or sulphuric acid, due to

his failing to overcome the difficulties connected with the state of extreme dilution, and also the very variable strength of the sulphuretted hydrogen generated.

Ludwig Mond in England and Mactear in Scotland worked upon similar lines, but their respective processes, though ingenious and theoretically sound, also failed to produce commercially applicable results.

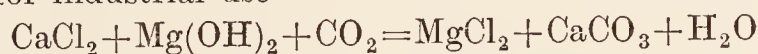
Schaffner and Helbig (*Eng. Pat.* March, 1878) worked out a process at Aussig in Saxon Switzerland, based upon the following operations:—

1. The decomposition of alkali waste by heating it with a solution of magnesium chloride



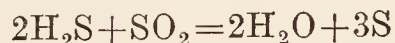
The magnesium hydroxide thus produced was found to be held in suspension by the calcium chloride.

2. Magnesium chloride was reformed by acting upon the suspended magnesium hydroxide with carbon dioxide, and the calcium chloride was converted into carbonate of lime available for industrial use



It was subsequently found by Frederick Chance that in this reaction, the average loss of magnesium chloride (calculated as magnesium) amounted to 1.05 parts per 100 parts of alkali waste operated upon.

3. The sulphuretted hydrogen gas liberated was treated for sulphur production with a view to effect the reaction



This had been previously attempted, but no satisfactory yield could be obtained owing to the formation of polythionic acids (*Debus, Chem. Soc. Trans.* 53, 278).

This formation Schaffner and Helbig endeavoured to prevent by causing the gases to react in the presence of a definite quantity of calcium chloride or magnesium chloride. By their process the necessary sulphur dioxide was obtained by burning one-third of the H_2S into SO_2 and steam, and this mixture was passed, together with the remaining two-thirds of the H_2S , up a tower filled with blocks of wood over and down which a solution of calcium chloride was caused continuously to trickle. The latter on issuing from the tower contained the free sulphur in suspension and it was subsequently recovered.

This process, although a great improvement upon what had previously been achieved, did not entirely prevent the formation of polythionic acids. Indeed, it was stated by Weldon that such formation amounted to nearly 10 p.c. of the total sulphur present, and that the maximum yield of free sulphur amounted to a very little over 80 p.e.

The process was taken in hand by A. M. Chance and his colleagues at their works at Oldbury and two years of experimental trials were devoted to it. As a result, it was proved that the production of sulphur, as such, by this process, did not constitute a commercial proposition owing to low yield, &c., but it was also proved that by burning all the sulphuretted hydrogen gas into sulphur dioxide it was possible to produce sulphuric acid at a price corresponding to 3*d.* per unit of sulphur per ton

of Spanish pyrites, whereas the price had been previously maintained at 6*d.* per unit. The process was industrially worked for some little time, but had to be stopped when the Tharsis Company reduced their price of pyrites to 3*d.* per unit and made contracts with alkali makers at this price extending over a period of years.

Undaunted by this reverse, Chance continued his work, and with the able assistance of H. W. Crowther and others he succeeded, four years later, in 1887, in producing sulphur at a price which permitted of competition with Sicilian brimstone. There can be no doubt that the adoption of this process by the Leblanc alkali makers was very largely responsible for their being able to continue the Leblanc as opposed to the Solvay ammonia soda process, and thereby avoid the scrapping of plant involving huge loss of capital. The process has been worked continuously since its introduction and is still employed by the Leblanc alkali makers. It is difficult to obtain accurate data as to the quantity of sulphur which has been thus produced, but from trustworthy information it may be stated that the minimum output has been about 35,000 tons per annum, mainly manufactured in Great Britain, and that therefore since the installation of the process it has yielded a minimum production of about 840,000 tons of sulphur.

The process, known as the Chance-Claus process, is based upon the lines followed by Gossage, of decomposing the calcium sulphide of vat waste by means of the carbon dioxide obtained from lime kilns and of recovering the sulphur from the sulphuretted hydrogen gas thus generated. But one of the essential features of success was to obtain both the carbon dioxide and the sulphuretted hydrogen gas in a state of concentration.

It had previously been found impossible to obtain lime-kiln gases containing more than an average of 30 p.c. of carbon dioxide, the remaining 70 p.c. consisting essentially of nitrogen. The presence of this latter obviously caused the dilution of the sulphuretted hydrogen and to such an extent that the economic production of sulphur was impossible. It was further found that the amount of sulphuretted hydrogen varied from 1 p.c. of the total gases up to not exceeding 35 p.c.

Chance succeeded in obtaining a constant yield of sulphuretted hydrogen of very high strength (Eng. Pat. 8666, 1887). This was effected by employing a series of communicating vessels provided with inlet and outlet mains. The vessels contained the alkali waste mixed with water in the form of cream to which a given proportion of caustic lime was, if necessary, added. The lime kiln gases, on being passed into the first vessel of the series, give up the carbon dioxide to the free lime present, forming calcium carbonate, and the sulphuretted hydrogen together with the nitrogen is passed on into the next vessel of the series. The sulphuretted hydrogen is then absorbed, calcium hydrosulphide (CaH_2S_2) being formed. This process of absorption is continued throughout the series, and as finally worked out acts so efficiently that the gas issuing from the last vessel contains only traces of sulphuretted hydrogen and carbon dioxide, the former being

recovered by passing through bog oxide or lime and the nitrogen allowed to escape into the air. The inlet and outlet mains are so devised that the respective vessels can be arranged in any order to constitute the series. In due course the carbon dioxide acts upon the calcium hydrosulphide formed as above described



The gas thus generated is mixed with sulphuretted hydrogen issuing from another vessel, and by suitable regulation of the vessels high strength of gas is obtained. The sulphuretted hydrogen is then conducted to a gas holder of about 30,000 cubic ft. capacity, escape of gas being prevented by the use of 'dead oil.' In practical working it has been found that the sulphuretted hydrogen thus conveyed to the gas holders contains about 2 p.c. of carbon dioxide. So long as there is no condensation of moisture on the plates of the gas holder, this amount of carbon dioxide will do no harm, but in presence of moisture the corrosion of the gas holder plates may become a serious matter. To ensure the absence of such moisture the gas holders should be placed a few hundred yards from the series of vessels, which are termed carbonators. The gas is conveyed to the holders through a 12-inch main and when leaving the carbonator it is distinctly warm; but by passing through say 300 yards of this main the gas is found to be cooled practically to atmospheric temperature before it enters the holder, and thus condensation in the holder itself is prevented. This precaution has been found to prolong the life of the holder very greatly and thereby to exercise a very important effect upon the economical working of the process.

The yield of sulphur obtained as sulphuretted hydrogen by this process may be taken as not less than 90 p.c. of the total sulphur contained in the vat waste.

Vat waste contains salts of soda, and when the decomposition as above described is completed these are found to be converted by the action of the carbon dioxide into sodium bicarbonate. This is ultimately recovered, because the mud which contains it is used for black ash making instead of chalk. In this way about 3 p.c. of soda calculated upon the alkali produced, which by the old method of working was lost, is recovered.

The concentrated sulphuretted hydrogen thus obtained is next treated with a view to the recovery of the contained sulphur by a process invented by C. F. Claus (Eng. Pats. 3608, 1882; 5070, 5958, 5959, 5960, 1883). This was originally devised for the recovery of sulphur from the sulphuretted hydrogen contained in coal gas, but it was recognised by Chance that it could be made applicable to the solution of one important part of the problem at which he was working. He therefore acquired the patent rights, and after four years' work at Oldbury, largely devoted to securing a continuous exact supply of the necessary quantity of air to decompose the sulphuretted hydrogen, success was achieved.

Anhydrous ferric oxide is used for the absorption of the sulphuretted hydrogen. This oxide is placed upon a bed within the kiln, which bed consists of broken fire brick or other

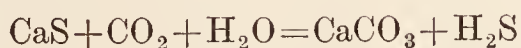
suitable chemically inert material. It is maintained at a temperature which keeps the ferric oxide at a dull red heat. This temperature results from the heat of the reaction, but it may if necessary be supplemented. The sulphuretted hydrogen mixed with the necessary quantity of air to bring about the formation of sulphur and steam is passed through the anhydrous ferric oxide: the volatilised sulphur together with steam pass out of the kiln into chambers where the sulphur is deposited. It may be obtained either as fused or sublimed sulphur, dependent upon the temperature of the kiln and of the depositing chambers. The ferric oxide undergoes no change and may be continuously used. The sulphur obtained by this process is of a high degree of purity.

The Chance-Claus process depends on a reaction originally observed by Gossage, who, in 1837, patented (Eng. Pat. 7416, 1837) a process in which the calcium sulphide of the alkali waste was decomposed by carbon dioxide.

Gossage himself failed to make the process technically successful.

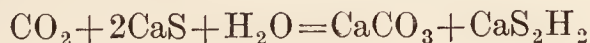
Since his time others, viz. Opl, Rawes (Eng. Pat. 1393, 1882), Claus (Eng. Pat. 5958, 1883), proposed processes depending on this decomposition.

The reaction is



The difficulty was to find an outlet for the sulphuretted hydrogen. The earlier efforts to utilise fuel gases or gases from inefficiently-worked lime-kilns with a low percentage of carbon dioxide gave a gas too weak in sulphuretted hydrogen to burn by itself.

Chance made use of lime-kiln gas from a more efficiently-worked lime kiln, and also showed the way to get a gas richer in sulphuretted hydrogen by taking advantage of the fact that the first reaction on carbonating a slurry of alkali waste is



This means that at first a portion of the carbon dioxide is absorbed, but no sulphuretted hydrogen is given off. By allowing the inert gases present with the CO_2 to pass away during this stage of the process a double equivalent of sulphuretted hydrogen is liberated in the final stage for each equivalent of carbon dioxide.



The Chance process is described in Eng. Pat. 8666, 1887, and in a lecture by Mr. A. M. Chance (J. Soc. Chem. Ind. 1888, 162).

The process was worked by Chance at Oldbury, and the gases enriched as above described contained about 33 p.c., or even 38 p.c. of sulphuretted hydrogen.

At first it was attempted to utilise the sulphuretted hydrogen as a source of sulphuric acid. The dilution and varying strength of the gas obtained, and a material drop in the price of sulphur in pyrites prevented this plan from succeeding economically. It was not until C. F. Claus published his patent 3608 of 1882 that Chance was able to develop his process on successful lines. Claus showed that it was technically possible to burn sulphuretted hydrogen under such conditions that the oxygen

combined with the hydrogen only, and the bulk of the sulphur could be obtained at once in a marketable form.

The reaction utilised by Claus is represented by the following equation: $\text{H}_2\text{S} + \text{O} = \text{H}_2\text{O} + \text{S}$.

Further Claus patents are Eng. Pats. 5070, 5958, 5959, and 5960, 1883).

The following is a description of the plant and method of work usually employed at present in carrying out the Chance-Claus process.

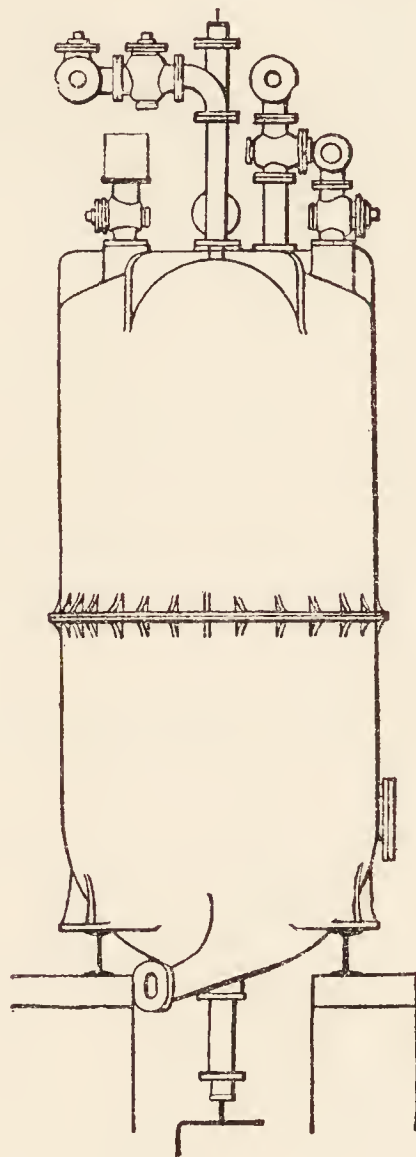


FIG. 1.

Alkali waste as fresh as possible is mixed with water into a cream of 1.2–1.25 sp.gr. in an iron vessel fitted with a mechanical agitator. From the mixer the waste is usually run into another similar vessel passing on the way through a coarse mesh sieve to remove cinders and lumps. The second vessel acts as a store, and is also fitted with a mechanical agitator to keep the waste from settling.

From this store tank the cream of waste is pumped by a large ram pump into a shute which feeds the series of carbonators in which the waste is treated with carbon dioxide.

The carbonators are strong cast-iron vessels, arranged usually seven in a series. Fig. 1 shows a carbonator.

The carbonators are cast in two parts, as shown above, and are usually about 7 ft. in diameter by 15 ft. high. The fresh lime-kiln gas is pumped first into the nearly spent carbonator, and then on through the series to the freshly-charged cylinder at the other end.

The somewhat elaborate pipe connections necessary to enable any one cylinder to act as a leading cylinder are shown in diagram in the patent specification of Chance and Chance

(Eng. Pat. 8666, 1887) and described in Chance's paper above referred to.

From the carbonators the issuing gas passes into a gas holder of considerable size. Chance's own gas holder was 50 ft. diameter with a 14-ft. lift and held about 30,000 cub. ft. of gas. The gas holder plays an important part in neutralising the fluctuations in the strength of the sulphuretted gas produced.

The working of the carbonators when the Chance enrichment process is used was described by Chance as follows:—

'At 7 P.M. Nos. 7 and 1 vessels (Fig. 2, where the discs represent the 7 carbonators of a series) were charged with fresh waste. The lime-kiln gases were pumped direct into No. 3 vessel, and then through vessels 4, 5, 6, 7, and 1 by opening all the intermediate taps; the useless gases escaped from No. 1 vessel into the exit main, and thence through a purifier into the air for a period of 1 hour 40 mins.

'At 8.40 P.M. the sulphuretted hydrogen gases from No. 5 vessel were sufficiently strong for use, the calcium sulphide having mostly been converted into calcium sulphhydrate; the sulphuretted hydrogen gases taken from No. 5 tested over 30 p.c. H_2S , while the useless gases from No. 1 tested only 1 p.c., thus showing that vat waste is a very efficient absorber of sulphuretted hydrogen.

'The connections were then altered so that the H_2S gases could be taken from No. 5 to the gas holder. No. 2 vessel containing the partially carbonated waste was put into series, and the lime-kiln gases were now pumped through Nos. 2, 3, 4, 5, the sulphuretted hydrogen gases from No. 5 continuing to be taken to the gas holder for a period of 2 hours 25 mins., till 11.5 P.M. It was then found that the sulphuretted hydrogen gases were under 30 p.c., and that Nos. 2 and 3 were carbonated so thoroughly that water filtered from the mud did not tinge lead paper; Nos. 2 and 3 were, therefore, emptied and recharged.'

Much difficulty was experienced in working the enrichment process when the Chance plants were started, and it has been in most cases abandoned.

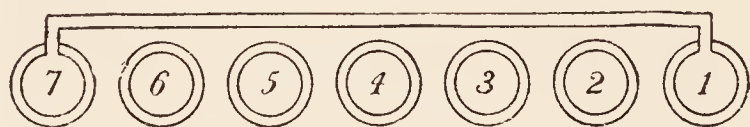


FIG. 2.

The following description shows, with the aid of the diagram Fig. 2, the method of working without enrichment.

No. 3 vessel is the leading carbonator into which the lime-kiln gases are first pumped, and is, therefore, the most nearly finished.

The gases pass from No. 3 through Nos. 4, 5, 6, 7, and 1 carbonators, No. 1 being the last charged, and from No. 1 to the gas holder.

No. 2 carbonator is empty and ready for recharging.

The lime-kiln gases are pumped into No. 3 carbonator until the liquor in it no longer blackens lead paper. No. 3 is then finished, and is disconnected, No. 4 becoming the leading cylinder. No. 2, which has in the meantime been refilled, is connected up to the series, and becomes the final cylinder from which the gases

pass to the gas holder under sufficient pressure (about 8 ins. water) to maintain the weight of the holder, and thus supply the pressure necessary to drive the gases on through the remainder of the plant.

It is usual to work the carbonators in 2, 3, or 4 sets of 7 vessels each in parallel, the number depending on the quantity of waste to be treated. By this means also the effects of the inevitable fluctuations in strength of the gas are materially reduced. Two such sets will deal with the waste from 300 tons salt-cake a week. It is obvious that the strength of the sulphuretted hydrogen produced, as well as the power consumed in pumping the lime-kiln gas through the carbonators, depends on the steady composition and percentage of carbon dioxide in the lime-kiln gases themselves.

Chance, in his lecture already referred to, gives great credit to Mond for his improvements in the working of lime kilns, and acknowledges the assistance received from him in this part of the process. Chance goes on to say, 'from the best-worked lime kiln, however, the escaping gases never contain on an average more than 30 p.c. CO_2 .'

Further experience in working has somewhat increased the amount of carbon dioxide in lime-kiln gas.

Two points about the lime-kiln gas in addition to its content of carbon dioxide are of great importance for this process.

1st. It is essential the gas should be practically free from oxygen, as oxygen in the gases pumped through the carbonates oxidises part of the sulphur in the waste to sulphite and thiosulphate, and prevents its recovery.

2nd. It is also important that the kiln gases should be practically free from carbon monoxide, because the combustion of this gas together with the sulphuretted hydrogen in the Claus kiln liberates additional heat, which, as will be seen later, reduces the efficiency of the Claus kiln.

We have now in the gas holder when working with a lime-kiln, gas containing 30 p.c. CO_2 , a gas which:—

1st. When enriched by Chance's nitrogen elimination process contains 30–33 p.c. H_2S .

2nd. When not so enriched contains about 25 p.c. H_2S . These figures, of course, depend on the valves that regulate the distribution of the gases to the carbonators being in good condition and not leaking.

The gas from the gas holder then passes through a small vessel called a mixer, into which a carefully regulated supply of air is pumped by a blower or fan, and then through a water lute into the Claus kiln.

Fig. 3 shows a section of an average-sized Claus kiln.

The kiln is made of wrought-iron plates, and is 25 ft. in diameter by 9 ft. deep. It is brick-lined, and has a table of perforated tiles on which the packing is placed.

1st. About 12 ins. of broken fire brick.

2nd. 12 to 24 ins. of bog iron ore. Water lutes act as safety valves in case explosion takes place.

The mixed gases, *i.e.* the gas from the holder and the air, pass through the water lute *b*, into the top of the kiln above the packing. The gases pass downwards and out through the exit pipe *h* into a cast-iron receiver *d*, Fig. 4,

which collects the bulk of the sulphur in a liquid form. The gases pass on from *d* into the brick chamber *e*, which contains several baffle walls, and in which almost all the remainder of the recoverable sulphur is collected as a coarse powder. The towers *f f* are very openly packed wooden scrubbers, which serve to collect an additional quantity of powdered sulphur. The Claus-kiln reaction is not complete, and always an appreciable proportion of the total sulphur passes away as sulphuretted hydrogen and sulphur dioxide with the exit gases.

From the exit *ff* it is usual to pass the gases through a furnace to burn the undecomposed sulphuretted hydrogen to sulphur dioxide before passing them on to the chimney.

Lunge states (Sulphuric Acid and Alkali, vol. iii. 11, 975) that of every 100 parts of sulphur entering the Claus kiln, 85 parts are recovered as refined sulphur and 15 p.c. is lost as sulphur dioxide and sulphuretted hydrogen, and polythionic acids.

This figure agrees very closely with the loss to be expected when the exit contains about 16 grns. S per cubic foot of gas, and the initial strength of the holder gas is 25 p.c. H_2S .

The bog-iron ore does not require renewal for many years, and has, in some cases, remained unchanged for over 20 years.

The working of the process is controlled by frequent tests of the exit gases from the Claus kiln for SO_2 and H_2S .

The method adopted is to obtain the total sulphur present, as SO_2 and H_2S , by drawing the gases through a known volume of standard iodine solution containing a little starch solution until the blue colour disappears, and noting the volume of gas aspirated.

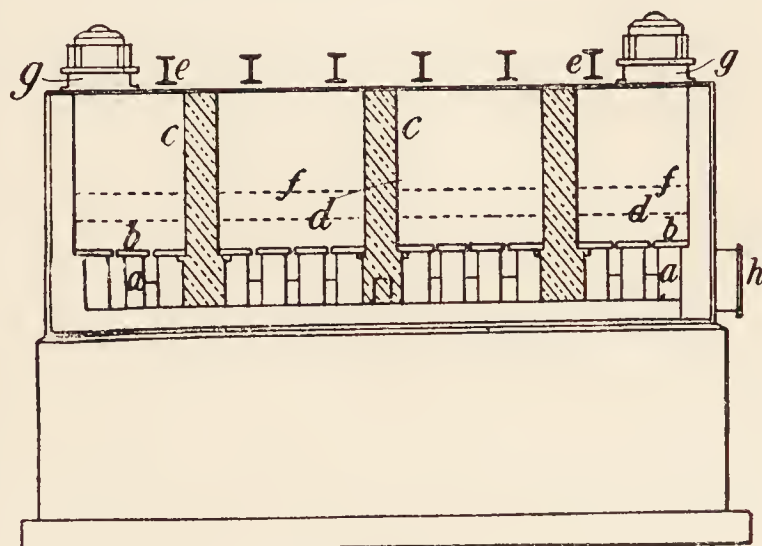


FIG. 3.

The actual sulphur dioxide in the gases is determined by drawing a known volume of the exit gases through water containing hydrogen peroxide and then titrating the sulphuric acid formed with standard soda solution, using methyl orange as indicator. The difference between the total sulphur per cubic foot and the sulphur present as sulphur dioxide is taken as

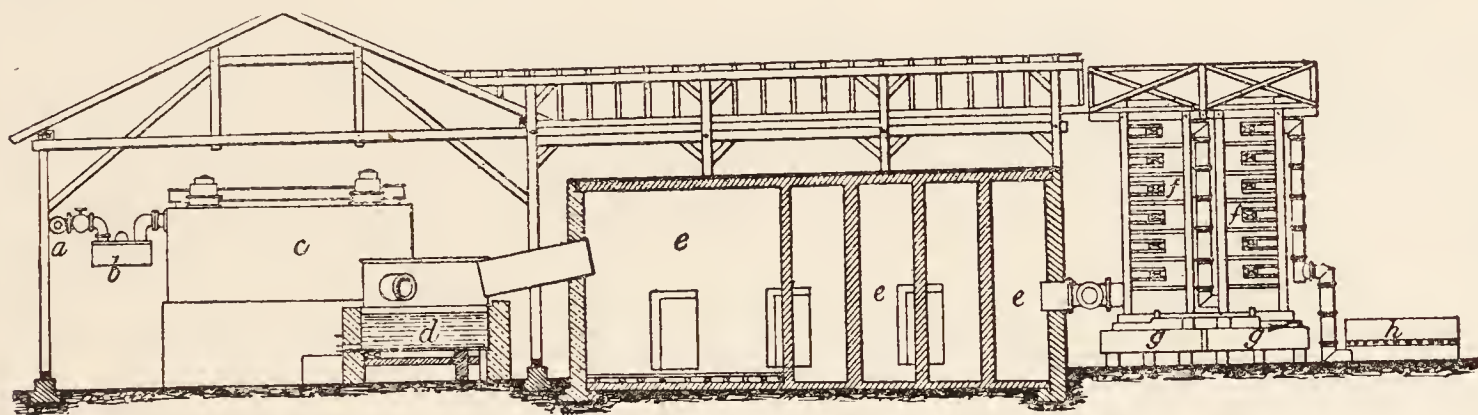


FIG. 4.

the sulphur present as sulphuretted hydrogen. The result in this country is usually expressed as grains total sulphur per cubic foot, and as grains sulphur as H_2S , and grains sulphur as SO_2 per cubic foot.

The air supply is adjusted in accordance with the relative proportion of sulphur as H_2S and SO_2 . If the mixture of gases is theoretically correct there should be obviously 2 H_2S to 1 SO_2 , that is to say, if the total exit is 15 grns. sulphur per cubic foot the sulphur as H_2S should be 10 grns., and as SO_2 5 grns. per cubic foot.

In practice it is usual to work with as nearly equal quantities of sulphur as H_2S and SO_2 per cubic foot as possible in the exit gases.

The efficiency of the sulphur recovery depends entirely on the regularity of these tests, and the care with which the air supply is regulated. The completeness of the reaction is largely affected by temperature. An increase in the Claus-kiln temperature is always followed by an increase in the exit tests, and in the proportion, therefore, of sulphur not recovered.

A Claus kiln, as above described, will make 15-20 tons of sulphur per week, but with 30

tons per week the temperatures are too high, and the exit tests materially raised.

With 15 tons sulphur per week the temperature of the exit gases taken 1 ft. from the kiln outlet is about $290^{\circ}C$., which may be considered a good working temperature.

A number of attempts have been made to improve the Claus-kiln action by substituting other materials for bog-iron ore. Bauxite is recommended by the Chemische Fabrik Rhénania and Projahn (Eng. Pat. 3122, 1906), and is now largely used. The Rhénania in Chem. Zeit. 1908, 249, states as the result of several years' trial of this substance that there is a material reduction in the Claus-kiln exit tests.

Titaniferous iron ore (Eng. Pat. 25976, 1907) and manganese dioxide have both been tried, but so far as is known have not been successful.

Many efforts have been made to utilise the sulphur in the Claus-kiln exit gases, and it has been suggested :

1st. To burn the exit gases completely to sulphur dioxide and pass them along with pyrites gases into vitriol chambers (see Alkali

Inspectors' 28th Report) and also through the Hargreaves salt-cake plant (see Alkali Inspectors' 29th and 30th Reports). The 38th Alkali Inspectors' Report states that all attempts to deal with Claus-kiln exits in vitriol chambers have been unsuccessful.

2nd. To burn the sulphur completely to sulphur dioxide and utilise it for production of sulphur trioxide by the contact process (Carey and Heslop, Eng. Pat. 10317, 1900).

This process has not been adopted.

3rd. By absorption in milk of lime and by the slurry from the carbonators, see Alkali Inspectors' Reports for 1903 and 1904, and Heaton, Eng. Pat. 21217, 1890.

With the improved exits obtained by careful working, especially when the bauxite packing is used in the Claus kilns, no difficulty is experienced in turning the exit gases, after complete burning in a furnace, into the atmosphere through a chimney without raising the SO_2 test of the chimney gases above the statutory limit.

We have still to deal with the contents of the carbonators after removal of the sulphur. These are calcium carbonate and a weak solution of soda salts, chiefly sodium bicarbonate.

The following analyses of the calcium carbonate and the carbonator liquor are given by Chance:—

Recovered calcium carbonate on dry	Water filtered from carbonator mud in grns. per gallon
Calcium carbonate 87.16	Soda (present as NaHCO_3) . . . 476.3
„ sulphate . 0.49	CaCO_3 . . . 124.3
„ chloride . —	Total S . . . 25.9
„ silicate . 2.3	S as SO_4 . . . 1.0
Magnesium carbonate 1.03	as hyposulphites 12.85
Sodium carbonate . 0.55	as sulphides . Nil
„ sulphate . 0.21	
„ silicate . 1.42	
Al_2O_3 . . . 1.47	
FeS . . . 0.71	
Coke . . . 2.06	
Sand . . . 0.56	

The recovered calcium carbonate contains all the CaCO_3 used in the revolver mixing, and Chance originally suggested its use in the revolver over again. Mason (Eng. Pat. 21314, 1901) proposes to mould the Chance process waste into blocks before use in the revolver.

As far as is known, however, the carbonator mud is not used in the revolvers at present.

Another proposition has been to utilise the Chance waste for the manufacture of Portland cement.

Chance waste has been actually used for this purpose by Rigby (J. Soc. Chem. Ind. 1890, 254), and for many years by Chance himself.

The Chance waste is also an excellent form of calcium carbonate for agricultural purposes, and is largely used in the districts surrounding the Chance sulphur recovery plants.

With the discovery and practical success of the Chance sulphur recovery process the Leblanc process was materially cheapened, and a complete cycle of processes created.

The sulphur in pyrites passes through the following series of steps, finally emerging as a very pure form of commercial sulphur. The sulphur starts in the pyrites, passes into sulphuric acid, into sodium sulphate, into black ash as calcium sulphide, into sulphuretted hydrogen, and finally into pure sulphur. The production, of course, varies with the efficiency of the plant, but the sulphur recovered represents 65–80 p.c.

of the sulphur in the salt-cake charged into the revolver.

Up to the present, the Louisiana deposit owned by the Union Sulphur Company practically supplies all the sulphur obtained in the United States. Endeavours have been made, and are still being made, to locate other deposits in the same geological formations and to organise their development.

Geological Survey of Louisiana, 2 vols., 1899 and 1902, U.S.A. Geological Survey; Zeitschrift Deut. Geol. Gesellschaft (Preussner), 1888, vol. xl. p. 194; Oil Fields of the Texas-Louisiana Gulf Coastal Plain, U.S.A. Geological Survey, Series A, Economic Geology, Bulletin No. 212, 1903; Mineral Industry, vols. 1 to date; The Journal of Industrial and Engineering Chemistry, Feb. 1912, pp. 132 *et seq.*, published by the American Chemical Society, containing—Geology of the Sulphur and Sulphur Oil Deposits of the Coastal Plain, by A. F. Lucas, p. 140; Sulphur Mines of the Union Sulphur Company in Louisiana, by F. H. Pough, p. 143.

During the war Germany required to pay much attention to the provision of elementary sulphur. Deposits of native sulphur are scarce in Germany, and those of Rybnick and Ratibor contain barely 10 p.c. Considerable amounts were obtained by reducing gypsum to calcium sulphide and burning the hydrogen sulphide obtained from this material to sulphur and water. The calcium sulphide was converted to hydrogen sulphide by magnesium chloride liquor (Schaffner and Helbig process) near Walbeck and at Bernburg, the magnesium chloride being obtained from neighbouring potash works. The gypsum (anhydrite) is broken up, dried, mixed with dry coal and heated in a revolving furnace to about 1100° . The product containing about 70 p.c. calcium sulphide is ground and treated with magnesium chloride liquor, and heated with steam. The hydrogen sulphide evolved is passed to a gasometer mixed with air and passed downwards through Claus furnaces, containing bauxite as contact material. The sulphur obtained is of 99.95 p.c. purity. The process is said to be still in operation, and likely to be in permanent use, as the sulphur so made is cheaper than the imported material (Zeitsch. angew. Chem. March 2, 1920; J. Soc. Chem. Ind. April 15, 1920, 134 R; cf. Riesenfeld, J. pr. Chem. 1920, [ii.] 100, 115).

Uses of sulphur.—Notwithstanding that the use of sulphur has practically become negligible in connection with the preparation of black gunpowder, and also that as it has, except to a very limited extent, been replaced by pyrites in the manufacture of sulphuric acid—the two industries which at one time accounted for the major portion of the consumption—there has nevertheless been a great increase in the world's annual requirements.

This is largely accounted for by the enormous development in the manufacture of paper from wood, due principally to the work of Ekman, Kellner and Partington. It is estimated that upwards of 180,000 tons of sulphur are yearly used in this connection, and that about 280 pounds of sulphur are required for every ton of wood pulp produced. The sulphur is used for the manufacture of the bisulphites of calcium and magnesium, but more particularly the former.

The bisulphite thus manufactured is added to the wood chips in a very dilute solution: indeed 5 p.c. of total SO_2 may be regarded as the maximum, and of this about 2 p.c. is purposely uncombined. It is essential that not more than traces of sulphuric acid be present, otherwise the pulp is injuriously affected. These two facts account for sulphur not having been replaced by pyrites in the manufacture of wood pulp bisulphites, because the dilute solution employed makes it practically necessary to manufacture the bisulphite where the wood pulp is made. The cost of transport per unit of sulphur available for conversion into sulphur dioxide is therefore a serious consideration. Moreover, it has not been found practicable to sufficiently limit the quantity of sulphuric acid present if the sulphurous acid is made from pyrites.

Sulphur is used to the extent of upwards of 100,000 tons per annum in Europe alone for preventing the growth upon the shoots and grapes of vines of the microscopic mould fungus *oidium*, which if allowed to develop causes the vine leaves to dry up: as a result, the grapes, when ripe, produce an unsound wine. The sulphur employed for this purpose is largely in the form of flowers of sulphur, although winnowed sulphur prepared as already described is also used.

The efficiency of sulphur as a preventive of the growth of *oidium* is considered to be largely dependent upon its physical condition. Thus, flowers of sulphur contain a certain proportion of amorphous sulphur which is much more easily oxidised than the crystals, even when in a very fine state of division. It is believed that by air exposure minute quantities of sulphurous acid and sulphuric acid are formed, which by their presence cause the destruction of the *oidium*. The question of the autoxidation of sulphur has been investigated by Windisch, August Harph (Zeitsch. anorg. Chem. 1904, 39, 387-388) and others, and from their work the conclusion as to the cause of destruction of the *oidium* would appear to be justified. In connection with the use of sulphur in viticulture, it should be pointed out that a very large quantity is used in addition to that mentioned above in the form of what is known as 'Bouillie Bordelaise,' which consists of a mixture of sulphur, copper sulphate, and various porous substances. The mixture is applied to the shoots and grapes of the vines.

Sulphur is also effectively used to prevent the growth of mould on hops. If the growth is not prevented the hops are practically useless. The mould in question is also an *oidium*, the species being similar to that found upon the vine. The fungus grows upon the upper and lower surfaces of the hop leaves, and if allowed to develop forms a white powdery spot on the 'burr' or buds of the hop cones. This stops the development of the cone into the hop, and hard, white knobs are formed which later on turn black. This black colour is due to mould, but when the hops get ripe a further variation in colour is apt to appear, known as 'red mould.' Flowers of sulphur are used as a preventive of hop mould. The total quantity used will vary from season to season, but on the average it is considerable.

Sulphur is also always burnt in the oast

houses when the ripe hop cones are being dried. For this purpose, 'rolled brimstone' is employed. The sulphur is burnt underneath the hops and fumes of sulphur dioxide are passed through the hops. The amount of sulphur thus employed averages about half a pound of sulphur per 10 bushels of green hops. The effect of the passing of sulphur dioxide through the hops is to bleach them, to improve their flavour, and to hasten the drying process (Amos, J. Inst. Brewing, 1910, 16, 142).

Sulphur is used upon a very considerable scale for the manufacture of bisulphite, mainly of calcium, employed as a preservative for fermented beverages, notably ale. It is also used for making sulphurous acid, which is employed to remove the smell of sulphuretted hydrogen which is liable to accumulate in wine barrels, and also to act as a disinfectant.

Sulphur is used in these cases because of its freedom from arsenic. The same remark applies to its application to the manufacture of sulphuric acid when the latter is required for the preparation of foodstuffs or pharmaceutical products. Sulphur is used in the treatment of cutaneous diseases, mostly in the form of ointments. It is also employed medicinally under the name of *milk of sulphur*, which is a precipitated amorphous powder prepared by precipitating the sulphur from a solution of calcium sulphide and thiosulphate by means of hydrochloric acid. Its medicinal properties are stated to be similar to those of sublimed sulphur only more active. Milk of sulphur should be completely soluble in carbon disulphide.

The purgative action of sulphur is probably due to the formation of hydrogen sulphide.

It has already been pointed out that one reason for employing sulphur instead of pyrites in the manufacture of bisulphite for wood pulp treatment is due to the great economy in transport per unit of available sulphur. The same argument holds good in connection with the manufacture of sulphuric acid employed in the making of high explosives for blasting purposes in South Africa, where sulphur is now used. A little more than 40 p.c. of sulphur is available for the production of sulphur dioxide calculated upon the weight of the pyrites whereas, 98 p.c. of available sulphur is derivable from brimstone.

Experiments indicate that flowers of sulphur will, in many cases, act as an efficient fertiliser. The addition of small quantities (0.023 gm. per kilo.) to the soil was found to materially assist the growth of carrots, beans, celery, lettuce, sorrel, endive, potatoes, onions, and spinach, the increase in the weight of the vegetables being, in some cases, as high as 40 p.c. and not lower than 10 p.c. It is suggested that the sulphur only acts indirectly by modifying the development of the soil bacteria. This view is based upon the fact that it was found useless when applied to sterilised soil. It is also asserted that sulphur exercises a favourable influence upon the development of chlorophyll, and plants grown upon a soil to which sulphur has been added are a much deeper green (E. Boullanger, Compt. rend. 1912, 154, 369-370, and A. Demolon, *ibid.* 1912, 154, 524-526; *ibid.* 1913, 156, 725).

The vulcanisation of rubber is effected by the addition under recognised conditions of

sulphur to india-rubber. Sulphur chloride, a solvent of sulphur, is used for vulcanising caoutchouc. The sulphur chloride of industry is a mixture of S_2Cl_2 and SCl_4 .

In the partition of sulphur between rubber and amyl or *n*-butyl alcohol, the relation between the concentration of the sulphur in the rubber and in the second medium is rectilinear; the sulphur is therefore dissolved in the rubber and not adsorbed by it. The solubility of sulphur in rubber can be determined by immersing strips in butyl alcohol which is maintained saturated with sulphur; after equilibrium has been attained the strips are removed and their content of free sulphur determined. The solubility of sulphur in grams per 1000 grms. of rubber is as follows, the bracketed figures indicating the degree of vulcanisation of the rubber used: at 40°, 14.8 (1.46), 15.3 (4.34), 16.9 (7.95); at 55°, 19.6 (0), 22.4 (2.98), 25.6 (6.54), 30.0 (13.92); at 75°, 32.2 (5.47), 42.5 (8.72), 59.0 (16.91). At 30° the solubility of sulphur is approximately 1 p.c., and is but slightly influenced by the vulcanisation coefficient, so that vulcanised rubber containing less than 1 p.c. of free sulphur should not "bloom" (*cf.* Skellon, J. 1913, 876; Venable and Green, J. 1922, 382 A; W. J. Kelly and K. B. Ayers, J. Ind. Eng. Chem. 1924, 16, 148; J. Soc. Chem. Ind. 1924, 43 B, 266).

Sulphur enters into the composition of certain cements. For this purpose, it is melted with iron filings and ammonium chloride; or, instead of melting the mixture, 100 parts of filings may be mixed with 5 to 15 parts of sulphur. To this mixture is added about 5 parts of ammonium chloride. The whole is then moistened with water and well mixed. Both mixtures yield cements useful for fixing glass to metal.

Sulphur is occasionally introduced into glass. The colours produced by it are due to molecular disperse sulphur present in the form of polysulphides: there is no evidence of the presence of colloidal sulphur (Fenaroli, Kolloid. Zeitsch. 1915, 16, 53).

Sulphur is also used in the manufacture of carbon disulphide, artificially made sulphides, hyposulphites, in the bleaching of silk and wool by means of sulphur dioxide, in the manufacture of ultramarine, and of artificial vermilion, and in the making of enamels.

A. G. S.

Allotropes of sulphur. Sulphur occurs in the crystalline, amorphous and plastic or soft conditions at ordinary temperatures, two of the crystalline forms being designated as α -S and β -S, and the insoluble amorphous or plastic variety as γ -sulphur. In view of the work of A. Smith and his co-workers, Aten and others, on liquid sulphur the solid must be considered in relation to various modifications of the liquid. Several allotropic varieties of crystalline sulphur are known, two of which, the rhombic and monoclinic, were described by Mitscherlich in 1823. Muthmann (Zeit. Kristall. 1890, 17, 336) examined four classes of crystalline sulphur, namely, the rhombic and three monoclinic forms. In addition to the foregoing we have Friedel's triclinic sulphur, Engel's rhombohedral sulphur, and a crystalline form described by Bichowsky (J. Washington Acad. Sci. 1919, 9, 126).

α -Sulphur consists of rhombic octahedra and

is the form in which this variety of sulphur occurs in nature. All the other varieties of sulphur are ultimately changed into this, which is the most stable form of sulphur, although the complete conversion may sometimes be delayed for years. Rhombic sulphur is formed from liquid sulphur below 98°, from saturated solutions in carbon disulphide, and by the oxidation of a solution of hydrogen sulphide in pyridine (Ahrens, Ber. 1890, 23, 2708). It is obtained from β -sulphur at a pressure of 5000 atmospheres (Spring, Wied. Ann. 1881, 5, 853) or from amorphous sulphur at a pressure of 6000 atmospheres (Threlfall, Brearley and Allen, Proc. Roy. Soc. 1894, 56, 37). Whilst at ordinary pressures molten sulphur yields prismatic or β -sulphur, at a pressure of 400 atmospheres octahedral crystals are obtained without the necessity of super-heating the liquid (Lowry, Chemical World, 1912).

β -Sulphur, monoclinic or prismatic sulphur, is deposited from hot solutions of sulphur in alcohol, benzene, chloroform, and turpentine. It is produced by heating liquid sulphur above 120°, allowing it to cool until a crust forms, piercing the crust and pouring the residual liquid through the hole thus formed.

Relation of α - to β -sulphur. Monoclinic sulphur is quite stable above 98°, but at ordinary temperatures it is slowly converted into rhombic sulphur. The change of 32.07 grms. of β -S to α -S is accompanied by the evolution of heat equivalent to 2.27 calories. As the change proceeds from the interior of a mass of crystal outwards, fissures and cracks are formed in the mass and the specific gravity rises from 1.982 to 2.038. The conditions of equilibrium between these two varieties of sulphur are dealt with in works on the 'Phase Rule' (*see* Findlay's Phase Rule, Longmans & Co.), the following being a short summary of the facts. At ordinary pressure and below 95.5° rhombic sulphur is the stable form, but above this temperature and up to 120° the monoclinic form is stable. For each additional atmosphere of pressure the temperature of the transition point is raised about 0.05° (Tammann, Wied. Ann. 1898, 88 (c), 633), and at 1288 atmospheres pressure the transition point is 151°. Above this temperature and pressure rhombic sulphur alone would crystallise from the liquid. Owing to the slow rate of transformation of α - into β -sulphur it is possible to heat α -S above the transition point of 95.5° up to the m.p. 114.5° (so called 'crystalline superheating'). Mere heating of α -S just above the transformation point is not sufficient to effect the change into β -S, but on contact with a crystal of β -S the transformation is rapid. On the other hand, the change of β -S into α -S proceeds rapidly at ordinary temperatures, and is accelerated considerably by exposure to light, vibration, scratching, contact with a crystal of α -S, or by the presence of carbon disulphide and other solvents.

Nacreous or mother of pearl sulphur is a form of monoclinic sulphur. It was obtained by Gernez (Compt. rend. 1884, 98, 144) by the slow diffusion of an aqueous solution of sodium thiosulphate into a solution of acid potassium sulphate. It is also prepared by heating sulphur with benzene at 140°, or by preparing a super-saturated solution in toluene, carbon disulphide, or alcohol in a sealed tube, and placing the end

of the tube in a freezing mixture; or by adding a solution of sulphur saturated in the cold to one prepared by heating. Nacreous sulphur occurs as pale yellow or almost colourless plates possessing a pearly lustre. It changes rapidly into rhombic sulphur. Another variety is obtained by diluting a solution of yellow ammonium sulphide with alcohol and keeping it in a tall glass cylinder at about 5°, or by mixing hydrogen persulphide with ether, alcohol or ethyl acetate. These forms are very unstable.

Triclinic sulphur is sometimes found in the upper part of vessels which have been used as sulphur heating baths, as in V. Meyer's vapour density apparatus. It is very difficult to preserve on account of the great tendency to pass into rhombic sulphur soon after cooling.

Rhombohedral sulphur (Engel, Compt. rend. 1891, 112, 866) is formed by cautiously adding strong hydrochloric acid at 10° or lower to a saturated solution of sodium thiosulphate, extracting with chloroform before any sulphur has had time to deposit from the aqueous solution, and then allowing the chloroform to evaporate spontaneously. Deep yellow or orange-coloured rhombohedral crystals are obtained (Aten's *Sφ*, see Zeitsch. physikal. Chem. 1914, 88, 321). After some hours the crystals change into insoluble amorphous sulphur, but if heated to the melting-point—below 100° in this case—they change into amorphous sulphur which is partly soluble in carbon disulphide.

Amorphous sulphur. Many varieties of amorphous sulphur are known, varying in hardness, plasticity, solubility in carbon disulphide, and stability. A form *soluble in carbon disulphide* is obtained by the spontaneous decomposition of hydrogen persulphide, the action of hydrochloric or sulphuric acid on alkali polysulphides, or the slow oxidation of aqueous solutions of sulphuretted hydrogen. When dissolved in carbon disulphide the solutions deposit rhombic sulphur.

Amorphous sulphur, which is insoluble in carbon disulphide, is converted into the soluble modification when heated, at about 100°, with an animal or vegetable oil, with a 10 p.c. solution of sodium sulphite, or with water alone. The insoluble sulphur does not dissolve in a cold 10 p.c. solution of sodium sulphite, and only a very small proportion dissolves in the boiling solution. Amorphous sulphur is completely soluble in a cold aqueous solution of sodium sulphide; and from the solution the soluble modification is obtained by precipitation with an acid or even by extraction with carbon bisulphide (R. Huerre, J. Pharm. Chem. 1923, 28, 223–232; J. Soc. Chem. Ind. 1923, 42, 1130 A).

Milk of sulphur, or lac sulphuris has been known for centuries. It is obtained by decomposing an aqueous solution of calcium polysulphide (obtained from flowers of sulphur and lime) by means of hydrochloric, sulphuric, or acetic acids. During the reaction sulphuretted hydrogen is evolved, and white or grey amorphous sulphur is deposited.

Flowers of sulphur consist of the condensed vapour formed in the cooler parts of the refining chamber used in the manufacture of sulphur. They are partly insoluble in carbon disulphide, and when freshly made contain at least 33 p.c.

insoluble sulphur. Domergue (Ann. Chim. anal. 1904, 9, 445) suggests that when less than this proportion of insoluble sulphur is present the product should be known as sublimed sulphur.

A peculiar feature of certain forms of amorphous sulphur is the fact that they are rendered insoluble by repeated evaporation with a solvent. This applies particularly to sulphur precipitated from sodium thiosulphate solutions by means of acids, to that obtained by the action of chlorine on hydrogen persulphide dissolved in carbon disulphide, and to sulphur formed by the decomposition of disulphur dichloride by water or alkalis. The soft forms of amorphous sulphur occur either as yellow liquids, or viscous masses. As a rule they harden slowly on keeping and more quickly on being stirred or kneaded, after which they are more or less insoluble in carbon disulphide. The oily varieties are miscible with carbon disulphide in all proportions, the solutions depositing rhombic sulphur. According to Brownlee (J. Amer. Chem. Soc. 1907, 29, 1032) all varieties of insoluble sulphur precipitated from polysulphides and thiosulphate are *S_μ* (see Smith and Holmes, J. Amer. Chem. Soc. 1905, 27, 797 and 979) i.e. a supercooled form of liquid sulphur. Precipitated 'soft amorphous sulphur' is crystalline according to Brownlee.

γ-Sulphur, the insoluble variety of amorphous sulphur, is obtained by heating sulphur to near its boiling-point and pouring a thin stream of the liquid into cold water. It always contains a little soluble sulphur, and when freshly made is an elastic substance which hardens after several days, and is then much more soluble in carbon disulphide. A solid form of γ-sulphur in the form of a glassy mass results from pouring the liquid into a mixture of solid carbon dioxide and ether or into liquid air. On allowing the temperature to rise the solid becomes elastic and can be drawn into thin threads. γ-Sulphur is also formed by various other methods: (1) the action of ultra-violet light on strong solutions of sulphur in carbon disulphide, (2) acting on molten sulphur with iodine or sulphur dioxide, (3) condensing sulphur vapour in water, (4) the incomplete combustion of carbon disulphide resulting from placing a cold tile in the flame, (5) the action of sulphur dioxide, ferric salts, fuming nitric acid and other oxidising agents on sulphuretted hydrogen. In all these cases a certain amount of soluble sulphur is mixed with the γ-sulphur. Some of the forms are very unstable and are easily rendered soluble on treatment with hot alcohol, sodium sulphide, sodium carbonate, and baryta solutions, but these varieties may be rendered more stable by means of sulphur dioxide, hydrochloric or sulphuric acids, and especially by disulphur dichloride, fuming nitric acid and other strong oxidising agents. The insoluble part of flowers of sulphur (*S_μ* in the light of recent work) behaves in this way, but it becomes soluble on prolonged heating with carbon disulphide. Spring (Ber. 1881, 14, 2579; and Bull. Acad. Belg. 2, 83) found that the insoluble varieties of sulphur were all converted into rhombic sulphur at a pressure of 8000 atmospheres.

The most stable form of γ-sulphur is obtained by the action of a large excess of water on disulphur dichloride or by the action of hot

aqueous soda on thiocarbonyl chloride. Berthelot found the latter to be almost completely insoluble in carbon disulphide, and it is only partially changed into soluble sulphur by prolonged boiling with alcohol. In general, insoluble sulphur is a fine light powder or a plastic solid and is insoluble in carbon disulphide and other solvents, except in so far as they convert it into rhombic sulphur. Smith and Holmes, however, have shown that amorphous sulphur dissolves slightly in carbon disulphide, and that the solubility is much increased by mixing it with soluble sulphur (*Zeitsch. physikal. Chem.* 1903, 42, 474).

Black sulphur. Mitscherlich (*J. pr. Chem.* 1856, 67, 369) proved that a trace of grease in molten sulphur is sufficient to affect the colour of the solid obtained from it. If sulphur is heated strongly in the presence of traces of such materials as wax, grease, and certain carbohydrates, it forms a dark, almost black, solid with a metallic lustre, as little as 1 in 500 of impurity being sufficient for the purpose. Black sulphur is also found in 'liver of sulphur' containing a little iron sulphide, but the colour persists when the iron is removed by potassium cyanide. On account of its extreme resistance towards reagents, and its marked insolubility, black sulphur has been considered a distinct variety (Knapp, *J. pr. Chem.* 1888, 38, (2), 48), but Neumann has shown that black Mexican sulphur is really yellow sulphur containing carbon (*Zeitsch. angew. Chem.* 1917, 30, 165), and points out that Knapp's material is probably mixed with carbon or a metallic sulphide. The existence of black sulphur as a distinct variety of sulphur is, therefore, not certainly established.

Blue or Green sulphur is formed on mixing a solution of ferric chloride with 100 volumes of sulphuretted hydrogen water, when the liquid assumes a deep blue colour which disappears as soon as the sulphur is deposited. Blue sulphur is best prepared by warming a solution of disulphur dichloride in benzene with cadmium chloride (*see also* Liesegang, *Zeitsch. Chem. Ind. Kolloide*, 1910, 7, 307, for a deep lilac-blue variety; and von Weinarm, *J. Russ. Phys. Chem.* 1915, 47, 2177, for various blue solutions of sulphur). When dried or treated with absolute alcohol, blue or green sulphur changes to pure yellow (Meyer, *Ber.* 1913, 46, 3089).

δ -Sulphur, or colloidal sulphur, was first prepared by Debus (*Ann.* 1888, 244, 88) by passing sulphuretted hydrogen through a strong aqueous solution of sulphurous acid kept at 0°, until all the sulphurous acid was decomposed. After a time the colloidal sulphur in solution is deposited in the form of yellow viscous drops which dissolve for the greater part when added to a large excess of water. Engel prepared colloidal sulphur from a solution of thiosulphuric acid containing free mineral acid which had been extracted with chloroform to obtain rhombic sulphur (*Compt. rend.* 1891, 112, 867). The aqueous portion deposited yellow flakes of sulphur which dissolved completely in water. Colloidal sulphur solutions have a bluish tinge and are unstable, but von Heyden has patented stable solid colloidal sulphur containing a small proportion of proteins (*D. R. P.* 164664 of 1905). The results of experiments on the coagulation of colloidal sulphur solutions, before and after

dialysis, by means of potassium chloride or bromide, show that the amount of the salt required to induce coagulation increases with the proportions of sulphuric acid and sodium sulphate present in the solution. Moreover, the quantity of potassium permanganate adsorbed is greater with the dialysed than with the non-dialysed colloidal sulphur solutions (G. Rossi, *Gazz. chim. ital.* 1924, 54, 65; *Chem. Soc. Abstr.* 1924, 126, ii. 404). According to Spring, colloidal sulphur is really a mixture of soluble sulphur and a hydrate of sulphur, $S_2 \cdot H_2O$, and not a special variety (*Rec. trav. chim.* 1906, 25, 253).

For purposes of lecture demonstrations colloidal sulphur may be prepared by pouring a hot saturated alcoholic solution of sulphur into about 100 volumes of water.

For a description of the preparation, purification, and physical properties of colloidal sulphur (sulphur hydrosols), *see* Sven Oden, *Zeitsch. Chem. Ind. Kolloide*, 1911, 8, 186, 9, 100; *Zeitsch. physikal. Chem.* 1912, 80, 709; *Nova Acta, Regiæ Soc. Sci. Upsala*, 1913, [iv.] 3, 1. Colloidal sulphur is capable of exhibiting various colours depending on the degree of dispersion, best shown by adding phosphoric acid to sodium thiosulphate solution (Auerbach, *Kolloid. Zeitsch.* 1920, 27, 223).

Liquid sulphur. Molten sulphur just above its melting-point is a pale yellow thin liquid, which on further heating becomes brown and viscous. The increase of viscosity begins at 160° and reaches its maximum about 180°, or 187° according to Rotinjan (Zeitsch. physikal. Chem. 1907, 61, 200). From this point up to about 260° the liquid remains brown and viscous; above this temperature it becomes thinner but remains dark.

Smith and Holmes (*l.c.*) show that there is a transition point about 160° (*cf.* Farr and Macleod, *Proc. Roy. Soc.* 1920, [A], 97, 80), and that there are two forms of liquid sulphur which are not apparently miscible in all proportions. One of these liquids, designated S_λ , predominates from the melting-point up to 160°, and the other liquid, S_μ , above 160°. The nomenclature S_λ and S_μ is sometimes retained for the solids derived from supercooled liquid sulphur, and for the forms of sulphur obtained by precipitation (Brownlee). S_λ and S_μ possess different degrees of solubility in triphenyl-methane and other solvents, that of yellow mobile S_λ increasing with rise of temperature, and that of brown viscous S_μ decreasing. It is known that when crystallised sulphur is heated, liquefied, and allowed to solidify the proportion of amorphous or insoluble sulphur increases with the temperature of the liquid, duration of heating, and rapidity of cooling. The amount of insoluble sulphur is also increased by passing sulphur dioxide or hydrogen chloride through the liquid, while it is diminished by ammonia gas, carbon dioxide, nitrogen, and sulphuretted hydrogen. The transition point of S_λ is, however, unaffected by the previous treatment of the sulphur, except in so far as sulphur which has been heated previously shows a distinct lag in the transition and does not become viscous so readily as rhombic sulphur. The transition is connected with a change in the molecular complexity, for Kellas deduced from his measurements of the

surface tension of liquid sulphur that the sulphur molecule between 117° and 157° is S_6 , and that a remarkable endothermic change occurs at 160° , from which temperature up to 445° the molecule is S_{18} (Chem. Soc. Trans. 1918, 113, 903).

Aten concludes that in addition to $S\lambda$ and $S\mu$ there exists $S\pi$, formed when $S\lambda$ is heated with disulphur dichloride (Zeitsch. physikal. Chem. 1912, 81, 257; 1913, 83, 442; 1913, 86, 17; 1914, 88, 321; and Proc. K. Akad. Wetensch. Amsterdam, 1918, 20, 824). Liquid sulphur is shown by Aten to give rise to at least three modifications of solid sulphur, viz. $S\lambda$ and $S\mu$ of A. Smith and his co-workers, and $S\pi$ which occurs in maximum proportion when sulphur is chilled from 180° . $S\phi$ is obtained by Aten when a strong solution of hydrochloric acid at 0° is added to a strong solution of sodium thiosulphate also at 0° and the liquid is extracted with toluene (this is Engel's rhombohedral sulphur). $S\pi$ and $S\phi$ differ in solubility and are distinct from $S\mu$, which is stated to be crystalline and not amorphous.

The degree of molecular complexity of liquid sulphur deduced from observations of its surface tension has been studied by Pisati (Gazz. chim. ital. 1877, 7, 357); Capelle (Bull. Soc. chim. 1908, [iv.] 3, 764); Zickendraht (Ann. Physik. 1906, [iv.] 21, 141); and more particularly by Kellas (Chem. Soc. Trans. 1918, 113, 903). According to Kellas at least 85 p.c. of mobile sulphur ($S\lambda$) between 115° and 160° has the constitution S_6 . The complexity alters above 160° , and an endothermic molecular polymerisation appears to occur near that temperature: $3S_6 \rightleftharpoons (S_6)_3$. This aggregate S_{18} seems to be stable up to near the boiling-point. The polymerisation may be due to a tendency in the sulphur to lower its valency with rise of temperature, the complex S_6 possessing a residual valency at 160° .

Molecular structure of sulphur. According to Beckmann (Sitzungsber. k. Akad. Wiss. Berlin, 1913, 886), cryoscopic measurements on solutions of naphthalene, diphenyl, aniline, quinoline, etc., in sulphur gave a value of 213 for the freezing-point constant, from which the latent heat of fusion is calculated to be 14.1 cal. Utilising the results of Smith and Holmes (Chem. Soc. Abstr. 1903, ii. 284), the molecule of amorphous sulphur is then found to be $S_{5.1}$, that is, it is probably S_6 . From various considerations the author comes to the conclusion that the molecule S_6 is dark brown, and hence he gives an explanation of the colour assumed by molten sulphur at different temperatures. The explanation involves the assumption of the formation of a complex between crystalline sulphur (S_8) and amorphous sulphur (S_6).

Boiling-point determinations on solutions of sulphur in liquid chlorine prove the existence of the chloride, S_2Cl_2 . When the light yellow solution of this compound is allowed to assume room temperature in a sealed tube, it becomes dark brown after a few hours, owing to the formation of the chloride SCl_2 .

Cryoscopic and ebullioscopic determinations on solutions of sulphur in bromine do not point to the formation of molecules containing only one atom of sulphur; only the bromide S_2Br_2 exists. Similar experiments in iodine solution

show that no combination takes place between sulphur and iodine.

Similar considerations apply to the cases of selenium and tellurium, which in other respects are analogous to sulphur (Chem. Soc. Abstr. 1913, ii. 858).

The *viscosity* of molten sulphur has the value 0.1094 C.G.S. units at 123° , and from this temperature it falls to a minimum of 0.0709 C.G.S. units at 150° , and then rises to 0.0759 at 159° , when the rise becomes more marked. Exposure to air in the molten condition, especially below 160° , has a marked effect upon the viscosity from 160° upwards, due apparently to the production of sulphuric acid (Farr and Macleod, Proc. Roy. Soc. 1920 [A], 97, 80).

All varieties of sulphur are apt to contain traces of sulphuric acid; flowers of sulphur contain the greatest amount; roll sulphur much less; colloidal sulphur remains almost as strongly acid after washing as washed flowers of sulphur. Powdered sulphur from different sources cannot be completely freed from acid by repeated washing, and it therefore appears probable that the acid is continuously formed by the action of air and moisture (Zänker and Färber, Chem. Zentr. 1914, ii. 1219).

Molecular weight.—This has been determined from the molecular surface energy of sulphur dissolved in carbon disulphide and disulphur dichloride (Pekar, Zeitsch. physikal. Chem. 1902, 39, 433), and found to correspond with S_6 or S_8 . Cryoscopic determinations in naphthalene and yellow phosphorus give S_8 for rhombic, monoclinic, and plastic sulphur. From the rise in the boiling-point of carbon disulphide and other solvents S_8 was found both above and below the transformation-point of rhombic and monoclinic sulphur. Timofejev (Centralblatt, 1903, 2, 1266) obtained the value S_6 in chloroform, S_8 in carbon disulphide, but in benzene no definite value was found, the results ranging from S_6 to S_{10} . In boiling tin tetrachloride and arsenic trichloride S_8 was found for rhombic, monoclinic, and plastic sulphur (Beckmann, Zeitsch. anorg. Chem. 1906, 51, 96). Aten arrived at the conclusion that $S\lambda$ is S_8 , $S\phi$ is S_8 , and $S\pi$ probably S_4 (Zeitsch. physikal. Chem. 1914, 88, 321). It is clear from the above that S_8 is definitely established and probably S_6 also under certain conditions.

The molecular weight of selenium in iodine has been found (Olivari, Chem. Soc. Abstr. 1909, ii. 39) to be Se_2 instead of Se_8 , whilst there is no indication of the presence of a compound (Pellini and Pedrina, Chem. Soc. Abstr. 1908, ii. 833). The low molecular weight is confirmed and is almost the same at 184° as at 104° . Sulphur gives values falling little below S_8 .

Anthraquinone (cryoscopic constant 148) gives S_8 and Se_8 , whilst diphenyl (ebullioscopic constant 59.3) gives similar values. It is therefore a specific influence of the iodine, and not of high temperature, that cause the dissociation of the selenium molecule.

Tellurium reacts with iodine, and the cryoscopic and ebullioscopic results indicate a large proportion of single atoms (Beckmann and Hanslian, Zeitsch. anorg. Chem. 1912, 80, 221; Chem. Soc. Abstr. 1913, ii. 402).

Vapour density.—Sulphur gives rise to a vapour consisting of complex molecules. Deville

and Troost (Compt. rend. 1863, 56, 891) obtained S_2 from 860° upwards. Biltz showed that even at the boiling-point of sulphur at ordinary pressures, some dissociation of S_8 molecules into S_2 takes place, and that the dissociation proceeds regularly up to about 900° when all the molecules are S_2 (Zeitsch. physikal. Chem. 1888, 2, 920; 1897, 19, 425). He also asserts that S_6 is not present in the vapour, since the density does not remain constant over any interval of temperature below 900° . From this temperature up to 1719° the value S_2 is obtained (Biltz and Meyer, Ber. 1899, 22, 725). Gerhard and Preuner calculated the equilibrium constants from the change of density at 448° with change of pressure, and concluded that S_4 or S_2 molecules are present (Zeitsch. physikal. Chem. 1903, 44, 733). Preuner and his co-workers also calculated that above 30 mm. pressure S_8 , S_6 , and S_2 are present in the vapour, and below this pressure possibly also S_4 .

The specific gravity differs with the form of the sulphur: amorphous sulphur 2.04, rhombic 2.06, monoclinic 1.96, rhombohedral 2.135 (the highest of all forms of solid sulphur), molten sulphur 1.801 to 1.815, and liquid sulphur at the b.p. (444.5°) 1.46 to 1.52.

Melting-point.—Rhombic crystals have a 'natural' m.p. of 114.5° and prismatic 120° . Beckmann and Platzmann (Zeitsch. anorg. Chem. 1918, 102, 201) pointed out that soon after fusion sulphur freezes at 119° , but when kept molten for some hours the freezing-point drops to the 'natural' f.p. 114.5° , indicating the presence of S_μ or S_π . Plastic sulphur has no definite melting-point, increase of temperature merely tending to convert it into crystalline sulphur (Kastle and Kelley, Amer. Chem. J. 1904, 32, 483).

Dried sulphur has been found to melt over a range of temperature from 116.8° to 118.5° (H. B. Baker, Chem. Soc. Trans. 1923, 123, 1223).

Boiling-point.—Sulphur is sensibly volatile at 100° and may be readily volatilised in a current of steam. Callendar and Moss (Proc. Roy. Soc. 1909, [A], 83, 106) found 444.55° for the boiling-point, and Eumorfopoulos (*ibid.* 1914, 90, 189) gave 444.61° on the thermodynamic scale. Chapuis also found 444.6° .

Mueller and Burgess (J. Amer. Chem. Soc. 1919, 41, 745) have given the following equation as representing the boiling-point at various pressures between 700 and 800 mm.:

$$t = 444.6 + 0.0910(p - 760) - 0.000049(p - 760)^2$$

If small pieces of rhombic sulphur are kept in contact with, or very near to, sheets of silver, copper, or lead, a circular sulphide film forms on the metal round the sulphur. Temperature, time, and presence or absence of light affect the result slightly. The effect is due to sulphur possessing an appreciable vapour pressure at the ordinary temperature. Silver, lead, or copper wire was wound round a quartz tube closed at one end, and containing sulphur. The whole was placed (open end inwards) inside a similar but larger tube. With dry air inside the apparatus, which was kept closed, no metallic sulphide formed at the ordinary temperature during nineteen months' exposure to light. With moist air a faint tarnishing was noticed (Chavastelon, Compt. rend. 1923, 177, 1040; Chem. Soc. Abstr. 1924, 126, ii. 37).

Specific heat.—Mean value between 0° and 100° is 0.1712.

Ignition temperature determined in a U-tube through which air is drawn is 261° at ordinary pressures, or 255° (uncorr.) and 257° to 264° (uncorr.) in oxygen (McCrae and Wilson, Chem. News, 1907, 96, 25). Moissan gives 275° – 280° in oxygen and 363° in air (Compt. rend. 1903, 137, 547). The differences between the two sets of results appear to be due to the different methods employed.

Phosphorescence.—Sulphur exhibits a feeble phosphorescent glow when heated in a current of air below its ignition temperature and the vapour passed through a cooled tube. The volatilised sulphur is thereby condensed in fine particles and their oxidation is attended by phosphorescence.

The heat of combustion when burning to sulphur dioxide is 71.08 cal. for rhombic, 71.72 cal. for monoclinic (Thomsen, Ber. 1880, 13, 959; and Thermische Unters, 2, 247), and 71.99 cal. for γ -sulphur (Petersen, Zeitsch. physikal. Chem. 1891, 8 609). The heat of evaporation found at $t = 396^\circ$ is 0.362 cal. (Traube, Ber. 1898, 31, 1562).

Electrical conductivity.—Pigulewsky, J. Russ. Phys. Chem. Soc. 1912, 44, 105.

Solubility.—Sulphur (except the colloidal variety) is practically insoluble in water, but dissolves in alcohol, ether, ethereal oils, and light petroleum, especially when the solvents are hot. Carbon disulphide dissolves 40 p.c. in the cold. Benzyl chloride dissolves 1 p.c. at 0° and 55.8 p.c. at 134° . Benzene and toluene dissolve about 26 parts of sulphur when hot. Rhombic sulphur dissolves readily in boiling acetic acid and methyl alcohol. The following figures for the weights of sulphur dissolved in 100 grms. of solvent are given by Delaplace (J. Pharm. Chim. 1922, [vii.] 26, 139). In chloroform at 15° , 0.374 grms.; in carbon tetrachloride at 15.5° , 0.645; in toluene at 20° , 1.857; in benzene at 15° , 1.582; in anhydrous ether at 13° , 0.188. Sulphur melts at 106.2° to 106.8° in contact with benzyl chloride, but only mixes with it in all proportions when a temperature of 136° is reached (von Bojuski, J. Russ. Phys. Chem. Soc. 1905, 37, 92).

The mode of combination of sulphur in certain organic (and inorganic) compounds can be distinguished by their behaviour towards sodium arsenite. Those which convert the arsenite into sodium thioarsenate, Na_3AsSO_3 , contain sulphur in the polysulphide form; these also convert cyanide into thiocyanate; those compounds which, through the intermediary action of water, oxidise the arsenite to arsenate, contain sulphur in the persulphide form, corresponding with the peroxide form of oxygen. Dixanthogen disulphide, diacetyl disulphide and cupric sulphide all belong to the first class; tin disulphide and ultramarine, however, contain sulphur only in the bivalent form and are not reactive. Diamyl disulphide, diphenyl disulphide, dithio-N-dimethylaniline and phenyl ethyl disulphide all oxidise arsenite to arsenate and are reduced to mercaptans; they contain one atom of persulphide sulphur. Methyl trisulphide with sodium arsenite gives both arsenate and thioarsenate, and is reduced to methyl mercaptan; it therefore contains one

atom each of polysulphide- and persulphide-sulphur. The free thiocyanogen of Söderbäck (A. 1920, i. 219) and the phenylthiolthiocyanate of Lecher and Wittwer (A. 1922, i. 641) both contain 1 atom of persulphide sulphur. When cupric thiocyanate is heated with sodium arsenite, a green precipitate is first formed which, on boiling, changes into red cuprous oxide, arsenate being formed. In acid solution, white cuprous thiocyanate and arsenate are formed. In this reaction, the formation of cuprous salt is not due to the reducing action of the arsenite; this is oxidised to arsenate by the thiocyanic acid formed when the cupric salt is heated (A. Gutmann, Ber. 1923, 56, [B], 2365; J. Chem. Soc. Abstr. 1924, 126, i. 134).

References.—In addition to those given above the following may be cited: Amorphous Sulphur, Smith and Holmes (Ber. 1902, 35, 2992); Amorphous Sulphur and its Relation to the Freezing-point of Sulphur, A. Smith (Proc. Roy. Soc. Edin. 1902, 24, 299); Causes which determine the Formation of Amorphous Sulphur, A. Smith (*ibid.* 1902, 24, 342); Change of State of Liquid Sulphur, Hoffmann and Rothe (Zeitsch. physikal. Chem. 1906, 55, 113); Vapour Pressures of Sulphur, Matthies (Chem. Zentr. 1906, 2, 204); Surface Tension of Fused Sulphur, Zickendraht (Ann. Chim. 1906, [iv.] 21, 141); Blue Sulphur, Paterno and Mazzucchelli (Atti R. Accad. Lincei, 1907, [v.] 16, i. 465); Thiozonides, Sulphur and its Organic Compounds, Erdmann (Ann. 1908, 362, 133); Equilibrium of Liquid Sulphur, Krut (Zeitsch. physikal. Chem. 1908, 64, 513; 1913, 81, 726); Solubility of Insoluble Sulphur, Wigand (Zeitsch. physikal. Chem. 1910, 75, 235); Effect of $S\mu$ on Transition Point of Monoclinic and Rhombic Sulphur, Smits and Lecuw (Proc. K. Akad. Wetensch. Amsterdam, 1911, 14, 461); Colloidal Sulphur, Meyer (Ber. 1913, 46, 3089); Beckmann, Paul and Liesche (Zeitsch. anorg. Chem. 1918, 103, 189); Constitution of Sulphur Vapour, Dobbie and Fox (Proc. Roy. Soc. 1919, [A], 95, 484).

J. J. F.

HYDRIDES OF SULPHUR.

Hydrogen sulphide or Sulphuretted hydrogen H_2S . This gas must have been known from very early times. It is described by the writers of the sixteenth and seventeenth centuries under the general name of 'sulphurous vapours.' Geber prepared milk of sulphur, but no mention is made of a foetid-smelling gas being given off in the process. Scheele was the first, in 1777, to examine the gas minutely, and its chemical composition was definitely established by Berthollet.

Occurrence.—Hydrogen sulphide occurs in the gases issuing from volcanoes, sometimes to the extent of 25 p.c. of their volume. It also occurs in the natural gas of Point Abino, Canada. Decaying vegetable substances, particularly the leguminous plants, peas, beans, and lentils, when heaped together in a moist condition evolve this gas, and it is also produced during the decomposition of animal substances such as blood, hair, flesh, &c. It is present in the hepatic waters of Harrogate, Aix-la-Chapelle, and other places. Decomposing organic matter

in contact with sulphates frequently generates this gas, and from this cause sulphides are occasionally found at the mouths of large rivers which bring down much organic matter. The smell of sewer gas is in part due to sulphuretted hydrogen, and this latter also occurs in coal-gas, from which it has to be removed by a special arrangement in gas manufacture.

For the conditions of reaction of hydrogen with sulphur leading to the formation of hydrogen sulphide, v. Hautefeuille (Compt. rend. 1867, 64, 610); Pelabon (*ibid.* 1897, 124, 686); Bodenstein (Zeitsch. physikal. Chem. 1899, 29, 315); Duham (*ibid.* 711); Norrish and Rideal (Chem. Soc. Trans. 1923, 123, 696, 1689, 3202). Combination appears to take place by way of two reactions, a gaseous reaction proportional to the pressure of the hydrogen, and a surface reaction independent of the pressure of the hydrogen. The temperature coefficient is 1.48 for the surface, and 2.19 for the gaseous reaction. The surface reaction is directly proportional to the internal surface of the vessel and independent of the quantity of sulphur. The heat of activation of the gaseous reaction is 52,400 calories, or exactly double that of the surface reaction, viz. 26,200 calories.

Norrish and Rideal (*l.c.*) suggest in explanation of this fact that the sulphur molecules can become activated in two stages.

Preparation.—(1) It is usually prepared by the action of dilute sulphuric acid on ferrous sulphide: $FeS + H_2SO_4 = FeSO_4 + H_2S$. It should be collected over hot water, in which it is less soluble than in cold. The gas obtained by this method is never pure, as the sulphide used contains small particles of metallic iron, which give rise to hydrogen. The gas should be washed in water to free it from acid or salt which may pass over. Excess of sulphuric acid causes the precipitation of white, anhydrous ferric sulphate which coats the sulphide and stops the evolution of gas.

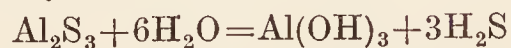
(2) A purer gas is obtained by heating antimony sulphide with hydrochloric acid of sp.gr. 1.1: $Sb_2S_3 + 6HCl = 2SbCl_3 + 3H_2S$. If native antimony sulphide be used, it should be first treated with dilute hydrochloric acid to decompose any carbonates which may be present.

(3) The gas may be prepared on a large scale by heating a mixture of equal parts of sulphur and paraffin, vaseline, or many other organic bodies.

(4) By heating a damp mixture of sulphur and charcoal.

(5) Hydrogen sulphide is formed together with sulphur dioxide when steam is passed over boiling sulphur, or even when sulphur is boiled with water: $3S + 2H_2O = 2H_2S + SO_2$. The two gases thus obtained mutually decompose one another, so that only a portion of the sulphuretted hydrogen remains, and sulphur is deposited.

(6) By the decomposition of aluminium sulphide by water

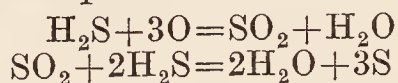


(7) By passing dry hydrogen over certain heated sulphides, such as powdered antimony sulphide: $Sb_2S_3 + 3H_2 = Sb_2 + 3H_2S$. The gas is also formed by passing a current of hydrogen through boiling sulphur; by burning a jet of

hydrogen in sulphur vapour, and by burning sulphur in an atmosphere of hydrogen.

(8) Pure H_2S may be prepared by passing the impure gas first through a drying apparatus and then through a series of vessels cooled by liquid air, in which it is solidified. When a sufficient amount has been collected, all residual gas is drawn out of the apparatus by means of a pump, and the condensed H_2S is then allowed to boil, the first 500 c.c. being rejected. The gas so obtained is completely absorbed by alkalis (Moissan, *Compt. rend.* 1903, 137, 363).

Properties.—Hydrogen sulphide is a colourless, inflammable gas, possessing a most disagreeable smell, resembling that of rotten eggs, which, when the gas has been prepared from ferrous sulphide, is due in part to volatile sulpho-carbon compounds derived from the iron. It has a sp.gr. of 1.1895 (Leduc), and 1 litre at 0° and 760 mm., weighs 1.5392 grms. It burns with a pale-blue flame, forming water and sulphur dioxide, and usually depositing more or less sulphur—



A mixture of two volumes of hydrogen sulphide and three volumes of oxygen explodes violently when an electric spark is passed through it, complete combustion taking place.

The gas when inhaled acts as a powerful poison, producing asphyxia; even in small quantities it causes sickness and headache. According to Thenard, an atmosphere containing $\frac{1}{800}$ of its volume of this gas will kill a dog, and smaller animals die with even less than that amount. An atmosphere with $\frac{1}{200}$ part of H_2S is sufficient to kill a horse, while cold-blooded animals are not affected by this proportion of gas. The best antidote is the inhalation of very dilute chlorine obtained by moistening a towel with dilute acetic acid, and sprinkling bleaching powder upon it.

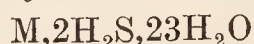
Hydrogen sulphide is soluble in water, one volume of this liquid dissolving about 4.4 volumes of the gas at 0° , and 3.2 volumes at 15° . The solubility at other temperatures is given by the expression

$$c = 4.4015 - 0.089117t + 0.00061954t^2$$

(Henrich, *Zeitsch. physikal. Chem.* 9, 435).

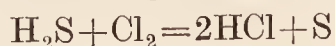
Alcohol dissolves 17.89 times its volume of the gas at 0° . The aqueous solution of the gas reddens blue litmus, and possesses the peculiar smell and taste of the gas. The solution decomposes on standing, the hydrogen combining with the oxygen of the air to form water, while sulphur deposits, imparting a milky appearance to the liquid. A solution of the gas in glycerol keeps better, and is occasionally used as a reagent.

A hydrate of hydrogen sulphide, of the formula $\text{H}_2\text{S} \cdot 7\text{H}_2\text{O}$, has been described by Forcrand (*Compt. rend.* 1902, 134, 281), and a series of mixed hydrates of the type



where M is a volatile organic halogen compound, have also been prepared.

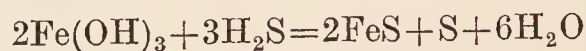
Hydrogen sulphide is decomposed by almost all oxidising agents. The halogens unite with its hydrogen, liberating sulphur



(The reaction with iodine only takes place in the presence of water.) Fuming nitric acid, dropped into a jar of the gas, decomposes it with explosive violence. Sulphuric acid is decomposed by H_2S forming S, SO_2 , and polythionic acids, hence the acid cannot be used for drying the gas. On account of its ready oxidisability, hydrogen sulphide is occasionally employed in organic chemistry as a mild reducing agent. It is easily decomposed by heat; according to Myers (*Annalen*, 159, 124) decomposition commences at a temperature of 400° . When a spiral of platinum is heated in the gas, sulphur is deposited and hydrogen liberated, which occupies the same volume as the original gas. The dissociation at various temperatures has been studied by Preuner (*Zeitsch. anorg. Chem.* 1907, 55, 279).

Hydrogen sulphide acts on most metals and many metallic oxides, forming sulphides; thus silver and mercury are immediately tarnished in contact with the gas. The sulphides are also formed when the gas is passed through solutions of many metallic salts as insoluble precipitates, several of which possess characteristic colours. Thus cadmium sulphide is yellow, antimony sulphide orange, and stannous sulphide chocolate-brown. Hence hydrogen sulphide is largely used in analytical operations, a current of the gas being passed through the solution under examination. Paper impregnated with a solution of a lead salt, *e.g.* the acetate, is used as a test for H_2S , such paper being blackened in contact with hydrogen sulphide. For the same reason, paintings containing white lead are darkened by exposure to the air of towns, while cards glazed with white lead, and engravings on paper whitened with that substance suffer similarly.

The hydrogen sulphide occurring in coal gas may be removed by passing the gas over hydrated ferric oxide



Hydrogen sulphide may be liquefied by pressure; its critical constants are $100.4^\circ \pm 0.1$ and 89.05 ± 0.1 atm. (Cardoso and Arni, *J. Phys. Chem.* 1912, 10, 504).

For vapour pressures *see* Cardoso (*Gazz. chim. ital.* 1921, 51, i. 153). The following tensions have been measured by Stock and Somieski (*Ber.* 1923, 56, [B], 247), on the gas prepared from iron sulphide and hydrochloric acid and purified by fractional distillation in a vacuum:—

-130°	3 mm.	-90°	117 mm.
-120°	7 "	-80°	247 "
-110°	20 "	-70°	440 "
-100°	54 "	-59.1°	778 "

The pure dry gas can be preserved unchanged over mercury. At the ordinary temperature a pressure of 17 atmospheres condenses it to a colourless, mobile liquid, of sp.gr. 0.9. The liquid boils at -61° , and freezes to an ice-like solid at -82.9° ; -83° and -60.2° (Cardoso and Arni); -83.6° and -60.0° (Maass and McIntosh). The density of the liquid at its b.p. is 0.964. Liquid H_2S can also be obtained by cooling the gas to about -70° with a mixture of solid carbon dioxide and ether, or by sealing up a quantity of hydrogen persulphide in one limb of a V-shaped glass tube. The persulphide

slowly decomposes, and the pressure eventually becomes sufficient to liquefy the hydrogen sulphide produced. The chemical activity vanishes almost entirely when the gas is liquefied; metallic potassium and sodium are unchanged in contact with the liquid, and it is also without action on chromates and permanganates.

Small amounts of H_2S in mineral waters may be detected by adding to the water a few c.c. of hydrochloric acid, stirring in a little solid *p*-aminodimethylaniline, and then adding a drop of ferric chloride. If H_2S be present a blue colour (methylene blue) will develop. This reaction will detect 0.018 mgm. of H_2S in a litre of water.

Salts.—A solution of hydrogen sulphide in water acts as a weak acid, whence the name sometimes given to it of 'hydrosulphuric acid.' It forms two series of salts, the sulphides R_2S and the hydrosulphides RHS . Of this latter class only the salts of the alkalis and alkaline earths are known; they are produced by the action of an excess of hydrogen sulphide on the oxides or hydroxides of these metals.

The normal sulphides can be obtained by the following methods:—

(1) By the direct union of a metal, *e.g.* Fe with sulphur at a high temperature.

(2) By the action of sulphur on certain metallic oxides, SO_2 being evolved.

(3) By the reduction of sulphates with carbon.

(4) By the action of CS_2 on some metallic oxides, *e.g.* Cr_2O_3 at about 250° .

(5) By the action of hydrogen sulphide on a metallic oxide or salt.

For the action of hydrogen sulphide on the alkyl oxides of the metals, *see* Rule (Chem. Soc. Trans. 1911, 99, 558). In each case reaction takes place in the cold, the products being alcohol and hydrosulphides of the metals.

Ammonium hydrosulphide, obtained by interaction of ammonia and hydrogen sulphide in dry alcohol or, better, in dry ether, forms white, crystalline needles. If excess of hydrogen sulphide be used, subsequent addition of ether saturated with ammonia precipitates a white, crystalline alcoholate of ammonium sulphide $(\text{NH}_4)_2\text{S} \cdot \text{C}_2\text{H}_5 \cdot \text{OH}$. If ethereal hydrogen sulphide be treated with excess of ammonia, addition of alcohol precipitates a yellow oil, $(\text{NH}_4)_2\text{S} \cdot 2\text{NH}_3$, with some transparent, apparently cubic, crystals supposed to be the normal sulphide, $(\text{NH}_4)_2\text{S}$ (J. S. Thomas and R. W. Riding, T. 1923, 123, 1181).

By the action of sulphur upon ammonium hydrosulphide in dry alcohol, orange-yellow crystalline ammonium pentasulphide, $(\text{NH}_4)_2\text{S}_5$, is obtained. On exposure to air, this pentasulphide becomes deep red, probably through formation of the heptasulphide, $(\text{NH}_4)_2\text{S}_7$, and finally decomposes to form hydrogen sulphide, ammonia, and sulphur; when heated in a sealed tube, it yields free sulphur and ammonium disulphide, $(\text{NH}_4)_2\text{S}_2$, as a yellow oil solidifying to a yellow, crystalline mass (J. S. Thomas and R. W. Riding, T. 1923, 123, 1726).

Besides the normal sulphides, many polysulphides of the type R_2S_2 , R_2S_3 , R_2S_4 , &c., exist. Those of the alkalis and alkaline earths can be prepared by boiling a solution of the

normal sulphide with an excess of sulphur. All the sulphides except those of the alkalis and alkaline earths are insoluble in water; many are decomposed by dilute acids with evolution of hydrogen sulphide. Many sulphides, *e.g.* those of lead, copper, and zinc, occur native as minerals and constitute important ores.

Uses.—Hydrogen sulphide is employed on the large scale to remove arsenic from sulphuric acid, for precipitating copper from solutions of the salts of that metal, and for precipitating gold and silver from waste material containing them. It is also largely employed in the laboratory in analytical operations.

Hydrogen disulphide H_2S_2 was discovered by Scheele in 1777, and more completely investigated by Berthollet. It was first obtained by pouring a concentrated solution of potassium pentasulphide into dilute, ice-cold hydrochloric acid, when, on standing for some time, yellow drops of a transparent, oily liquid separated out. Berthollet believed it to be analogous in composition to the potassium sulphide used in its preparation, and assigned to it the formula H_2S_5 . Thenard, however, who found it possessed many properties in common with hydrogen dioxide, gave it the formula H_2S_2 , though his analyses always showed a larger proportion of sulphur than is demanded by this formula. Hofmann, who obtained it by decomposing with hydrochloric acid a crystalline compound formed by the action of ammonium persulphide on strychnine, believed it to possess the formula H_2S_3 . It has been shown that the so-called 'hydrogen persulphide,' hitherto obtained is really a mixture of a di- and tri-sulphide (Schenck and Falcke, Ber. 1908, 41, 2600).

Preparation.—A solution of sodium or calcium polysulphide is carefully poured into an equal volume of concentrated hydrochloric acid, kept well cooled by ice. A heavy, yellowish oil separates out, which is then submitted to distillation under reduced pressure. The di- and tri-sulphides are separated by fractional distillation. Care must be taken to remove all traces of alkali from the distillation apparatus by previously treating it with sulphuric acid, as the hydrogen persulphides are very readily decomposed by even traces of alkali.

For further details, *see* Walton and Parsons, (J. Amer. Chem. Soc. 1921, 43, 2539).

The disulphide thus obtained is a colourless oil, boiling at 74° – 75° (2 mm.), of sp.gr. 1.376. It melts between -88° and -90° , but has no sharp point of solidification. It is more volatile than the trisulphide, and not so readily attacked by alkalis.

Hydrogen trisulphide H_2S_3 . Hydrogen trisulphide forms a yellow strongly refracting liquid of sp.gr. 1.496 at 15° . On cooling it becomes colourless. It boils at 43° – 50° ($4\frac{1}{2}$ mm.), and solidifies at about -53° . It has an odour resembling that of camphor and sulphur monochloride. Its vapour is irritating. It decomposes slowly in the dark, more rapidly on exposure to light, evolving H_2S and depositing sulphur. It dissolves in many organic solvents without decomposition, and its solutions in ether, benzene, and carbon disulphide are relatively stable (Schenck and Falcke, *l.c.*).

Metallic oxides and alkalis decompose it, some so violently as to cause it to ignite. It forms a well-crystallised compound with benzaldehyde of the composition $(C_6H_5 \cdot CHO)_2 \cdot H_2S_3$ (Brunner and Vuilleumier, Chem. Zentr. 1908, ii. 588).

Both hydrogen disulphide and hydrogen trisulphide dissolve large quantities of sulphur, and the variation of solubility with temperature shows a well-defined break at -1.45° when the composition of the liquid phase approximates very closely to that of hydrogen hexasulphide, H_2S_6 (J. H. Walton and E. L. Whitford, J. Amer. Chem. Soc. 1923, 45, 601; Chem. Soc. Abstr. 1923, 124, ii. 315).

HALOGEN COMPOUNDS OF SULPHUR.

The affinity of sulphur for the halogens decreases from fluorine to iodine. The hexafluoride is a very stable compound, while the only well-defined chloride is S_2Cl_2 , the tetrachloride being easily decomposed. At the same time there is evidence for the existence of loosely combined polythionic chlorides in solution, although these compounds have not been isolated. The only known compound of sulphur and bromine has the formula S_2Br_2 , whilst no iodide is known, all the compounds previously classed as such (with the possible exception of S_3I_2) being merely mixtures of sulphur and iodine.

Sulphur hexafluoride SF_6 . This substance was discovered in 1900 by Moissan and Lebeau, who obtained it by the direct union of sulphur and fluorine (Compt. rend. 1900, 130, 865). It possesses a theoretical interest as being the first hexahalogen derivative of sulphur to be prepared. It is a colourless, inodorous, incombustible gas, condensible to a liquid at a low temperature (b.p. about -57°). It is slightly soluble in water, rather more so in alcohol. Chemically, it is a very inert body, but it is slowly decomposed when mixed with hydrogen and submitted to a powerful spark discharge, producing HF, H_2S and S, and it is also attacked by sodium or calcium vapour at a red heat.

Disulphur difluoride. According to Cennerszwer and Strenk (Ber. 1923, 56, [B], 2249), when a mixture of well-dried silver fluoride (1 grm.) and sulphur (4 grms.) is heated in a vacuum, a gas (about 100 c.c.) is evolved which does not condense at the ordinary temperature, and is believed to be disulphur difluoride, S_2F_2 . The surface of the mercury becomes blackened owing to the formation of mercuric sulphide. On exposure to the atmosphere, sulphur is deposited from the gas.

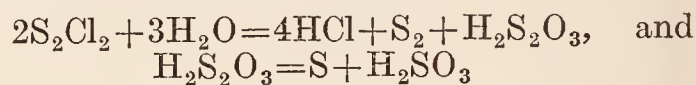
The molecular weight of the gas calculated from the density was found to be about 97.33 (mean of two experiments), and on analysis by absorption in a solution of potassium hydroxide and hydrogen peroxide, the following figures were obtained: S, 64.04 p.c., F, 35.17 p.c. It is assumed that the discrepancies were due to the presence of a little sulphur dioxide, as the gas has not yet been obtained quite pure; it is also formed on heating mercurous fluoride with sulphur. The gas is colourless and has an odour similar to, but even more objectionable than, that of disulphur dichloride. It is at once decomposed by moisture with deposition of sulphur (Chem. Soc. Abstr. 1924, 126, ii. 167).

Sulphur chlorides. Three chlorides of sulphur are known, i.e. S_2Cl_2 , SCl_2 and SCl_4 . Both the higher chlorides are readily dissociated into the monochloride and chlorine (Ruff and Fischer, Ber. 1903, 36, 418; Beckmann, Zeitsch. physikal. Chem. 1909, 65, 289; Bergmann and Bloch, Ber. 1920, 53, [B], 977).

Sulphur monochloride S_2Cl_2 or $Cl \cdot S \cdot S \cdot Cl$ was first obtained by Hagemann in 1781, but its composition was not fully established until the year 1810, when it was studied by Davy and Bucholz.

Preparation.—Sulphur monochloride may be obtained by passing dry chlorine gas over melted sulphur, and distilling the chloride from the excess of sulphur. The chlorine is generated in the ordinary way, and passed through a wash bottle containing water, then through calcium chloride, and thence over melted sulphur contained in a retort. The chloride of sulphur is condensed in a receiver cooled by a stream of cold water. On the large scale, sulphur monochloride is obtained as a by-product in the preparation of carbon tetrachloride from carbon disulphide and chlorine: $CS_2 + 3Cl_2 = CCl_4 + S_2Cl_2$.

Properties.—Sulphur monochloride is an amber-coloured liquid which fumes strongly in moist air, and possesses a peculiarly penetrating smell, its vapours attacking the mucous membrane. Its sp.gr. is 1.70941 at $0^\circ/4^\circ$ (Thorpe), m.p. -75° to -76° (Beckmann), and b.p. 138.1° . It is slightly decomposed on distillation under ordinary pressure, the first running being invariably red (*see* Dalzell and Thorpe, Phil. Mag. 1871, 309). Water slowly decomposes it, forming at first sulphur, hydrochloric acid, and thiosulphuric acid, this latter further splitting up into sulphur and sulphurous acid



Sulphur monochloride is miscible with benzene and carbon disulphide. It readily dissolves sulphur, and the saturated solution contains at ordinary temperatures 66.7 p.c. of sulphur. It acts on many metals, e.g. iron, tin, aluminium, and mercury, especially in presence of dry ether, producing chlorides (Nicolardot, Compt. rend. 1908, 147, 1304; Domanicki, J. Russ. Phys. Chem. Soc. 1916, 48, 1724), and most metallic oxides yield chlorides when heated in its vapour. This latter reaction affords a means of preparing certain chlorides free from oxychlorides (Bourion, *ibid.* 1909, 148, 170). Sulphur monochloride acts on many organic compounds to form sulphur derivatives; for example, with benzene it yields (in the presence of aluminium chloride) phenyl sulphide $(C_6H_5)_2S$. This reaction affords support to the formula $S = SCl_2$ for the chloride (Böeseken, Chem. Soc. Abstr. 1905, i. 583). The action of sulphur monochloride on aniline in cold dilute ethereal solution yields aniline hydrochloride and N-dithiophenylamine $C_6H_5N \begin{smallmatrix} S & S \\ \diagdown & / \\ S & S \end{smallmatrix} N \cdot C_6H_5$, the sulphur analogue of nitrobenzene (Coffey, Rec. trav. chim. 1921, 40, 747). Hicks (J. Amer. Chem. Soc. 1911, 38, 1492) has utilised sulphur monochloride for the decomposition of minerals containing rare earths, by heating them in a current of the vapour.

By adding an ice-cold chloroform solution of ammonia to sulphur monochloride in the same

solvent, nitrogen sulphide is obtained according to the equation :



Other sulphides of nitrogen, however, are formed, for after precipitation of the sulphide, N_4S_4 , by the addition of alcohol, the mother-liquors may be concentrated to obtain nitrogen pentasulphide, N_2S_5 , and also *hexasulphamide*, S_6NH_2 , which crystallises in colourless, square plates, m.p. 105° , insoluble in water, but soluble in organic solvents. This compound gives a coloration with alcoholic potassium hydroxide and with alcoholic solutions of organic bases. It is thought that this coloration may be due to the formation of a salt of a nitrogen-sulphur acid, but attempts to obtain such an acid or its salts were unsuccessful (Alexander Killen Macbeth and Hugh Graham, *Proc. Roy. Irish Acad.* 1923, 36, 31-40; *J. Chem. Soc. Abstr.* 1923, 124, ii. 855).

Uses.—Sulphur monochloride is used in defecating cane-juice and refining sugar, in the so-called Eastes' process. Its principal application is, however, for vulcanising india-rubber.

The articles to be vulcanised are first coated with india-rubber in the usual way, and are then placed in a closed chamber in which sulphur chloride is vaporised, by which means the vulcanisation of the india-rubber is effected (Abbot, *Eng. Pat.* 1878, 166).

Parkes' process, which has been in use since 1846, consists in immersing the india-rubber goods in a solution of sulphur chloride (saturated with sulphur) in carbon disulphide or benzene for a short time. It is used extensively in preparing the surface of tobacco pouches, tubing, rings, &c.

For a method of examining sulphur chloride for vulcanising work, see Frank and Marckwald (*Gummi-Zeit.* 1914, 28, 1580).

Sulphur dichloride SCl_2 is formed by passing chlorine into the cooled monochloride, containing about 1 p.c. of finely powdered charcoal, which, as a catalyst, facilitates the reaction between the chlorine and the monochloride (Pope and Heycock, *Eng. Pat.* 142879). See Hübner and Gueront. (*Zeitsch. für Chemie*, No. 15, 1870, 455); Dalzell and Thorpe (*Phil. Mag.* 1871, 309). It can only exist at a low temperature.

Sulphur tetrachloride SCl_4 . Sulphur tetrachloride is formed by saturating the monochloride with chlorine at a temperature of -20° . It forms a brown-red liquid, which on being strongly cooled freezes to a yellowish-white solid, of m.p. -31° . On removal from the freezing mixture the tetrachloride at once commences to decompose, evolving chlorine. Water decomposes it violently, forming sulphurous and hydrochloric acids $\text{SCl}_4 + 2\text{H}_2\text{O} = \text{SO}_2 + 4\text{HCl}$.

Sulphur tetrachloride forms well-defined crystalline double chlorides with many metallic chlorides, such as $\text{SbCl}_6\text{SCl}_4$, $\text{FeCl}_3\text{SCl}_4$, &c. (Ruff, *Ber.* 1904, 37, 4513).

Sulphur bromide. Sulphur monobromide S_2Br_2 is formed by direct union of its elements when sulphur is dissolved in a slight excess of bromine, and the excess of the latter then removed by a current of dry CO_2 . It is a ruby-red liquid, which boils at about 210° , and can be completely separated into its constituents by

repeated distillation. Water decomposes it in a similar manner to S_2Cl_2 . Caustic potash acts on it, giving a mixture of potassium bromide and sulphite with liberation of sulphur.

Determinations of the melting-points and vapour densities of mixtures of S_2Br_2 and bromine have failed to show the formation of any other compounds of bromine and sulphur (Ruff and Winterfeld, *Ber.* 1903, 36, 2437).

Sulphur iodide. A compound of the composition S_3I_2 has been described as obtained by the action of sulphuretted hydrogen on a solution of iodine chloride, the current of gas being stopped before the whole of the chloride was decomposed (MacIvor, *Chem. News*, 1902, 86, 5).

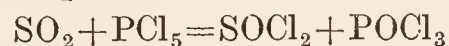
Other observers have, however, made detailed studies of the system sulphur-iodine, and rendered it probable that the above body is really only a mixture of sulphur and iodine, as no evidence of the formation of any compounds of the two elements could be obtained; see Boulouch, *Compt. rend.* 1903, 136, 1577; Smith and Carson, *Zeitsch. physikal. Chem.* 1907, 61, 200; Ephraim, *Zeitsch. anorg. Chem.* 1908, 58, 338; Olivari, *Chem. Soc. Abstr.* 1909, ii. 37; Wright, *Chem Soc. Trans.* 1915, 107, 1527.

OXYHALOGEN COMPOUNDS OF SULPHUR.

Two series of compounds of this class are known, corresponding to the two oxides of sulphur SO_2 and SO_3 . The former class are termed thionyl, and the latter sulphuryl compounds.

Thionyl fluoride SOF_2 , prepared by heating arsenic fluoride with thionyl chloride in a sealed tube at 100° , is a colourless gas with an odour like carbonyl chloride, liquefying at -32° . Water decomposes it into hydrofluoric and sulphurous acids.

Thionyl chloride SOCl_2 was first obtained in an impure state by Persoz and Block, and more fully investigated by Carius. It may be prepared by the action of dry sulphur dioxide on phosphorus pentachloride :



Other methods of preparation consist in the action of PCl_3 on thiosulphates, sulphites, and dithionates, and the direct union of chlorine monoxide with sulphur dissolved in carbon disulphide. Also by the reaction of sulphur or sulphur chloride with chlorine and chlorosulphonic acid, or of sulphur dichloride with chlorosulphonic acid, with or without the addition of a catalyst such as antimony trichloride or mercuric chloride. It may also be produced by the interaction of sulphur trioxide and sulphur dichloride at the ordinary temperature in presence of the chlorides of the heavy metals (Farbw. vorm. F. Bayer & Co., *Eng. Pat.* 27830, 1913; D. R. P. 275378).

Carbonyl chloride, or a mixture of carbon monoxide and chlorine, reacts with sulphur dioxide above 200° in presence of charcoal with formation of thionyl chloride and sulphur tetrachloride: $\text{SO}_2 + \text{COCl}_2 = \text{SOCl}_2 + \text{CO}_2$ and $\text{SO}_2 + 2\text{COCl}_2 = \text{SCl}_4 + 2\text{CO}_2$. The first reaction predominates at lower temperatures and with excess of sulphur dioxide; by suitable adjustment of conditions one or other of the reactions

may be almost entirely excluded (Chem. Fabr. Buckan, D. R. P. 284935).

Thionyl chloride is a colourless, strongly-fuming, pungent-smelling liquid, of sp.gr. 1.675 at 0°. It boils at 78°, and on heating to 440°, splits up into sulphur monochloride, sulphur dioxide, and chlorine. Water decomposes it, giving sulphurous and hydrochloric acids. It acts on oxygen acids as a chlorinating agent; thus with sulphuric acid it yields chlorosulphonic acid. On account of the ease with which it parts with its chlorine it is employed in organic chemistry in preparing chloro derivatives from certain hydroxy acids. It also acts on many organic aldehydes, *e.g.* piperonal, forming dichlorides, but the method is not of general application (Hoering and Baum, Ber. 1908, 41, 1914). Thionyl chloride may be made technically by adding SO₃ to S₂Cl₂ at a temperature of 75°–80°: $\text{SO}_3 + \text{S}_2\text{Cl}_2 = \text{SOCl}_2 + \text{SO}_2 + \text{S}$. Chlorine is passed continuously into the product to reconvert the sulphur into chloride; a nearly theoretical yield of thionyl chloride can thus be obtained (Chem. Fab. Griesheim Elektron Chem. Soc. Abstr. 1903, ii. 420). For its action on metals and metalloids, *see* North and Hageman, J. Amer. Chem. Soc. 1912, 34, 890; North and Thomson, *ibid.* 1918, 40, 774.

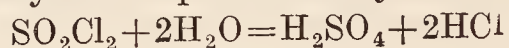
Thionyl bromide SOBr₂ has been prepared from thionyl chloride and sodium bromide by Hartog and Sims (Chem. News, 1893, 67, 82). It is an orange-yellow liquid, boiling at 68°, and of sp.gr. 2.61 at 0°.

Thionyl chlorobromide SOBrCl, prepared from thionyl chloride and hydrobromic acid, is a clear yellow liquid of sp.gr. 2.31 at 0°, boiling at 115° with slight decomposition (Besson, Compt. rend. 1896, 122, 320).

Sulphuryl fluoride SO₂F₂ is obtained by the direct union of sulphur dioxide and fluorine. It is more easily prepared by heating barium fluorosulphonate which, at a red heat, is decomposed into sulphonyl fluoride and barium sulphate. It is a gas, colourless and odourless, which liquefies at –52°, and solidifies at –120°. It dissolves in water without undergoing decomposition, and attacks glass. Alkalis decompose it, forming sulphuric and hydrofluoric acids (Moissan and Lebeau, Compt. rend. 1901, 132, 374).

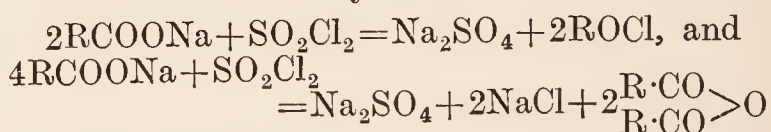
Sulphuryl chloride SO₂Cl₂. This body was discovered by Regnault in 1838, who obtained it by acting with chlorine on a mixture of ethylene and sulphur dioxide. It is best prepared by passing well-dried chlorine and sulphur dioxide simultaneously into a large glass flask containing some camphor which has previously been saturated with sulphur dioxide. Care must be taken that the chlorine is never in excess. The two gases combine to form sulphuryl chloride, the camphor remaining unaltered. The two gases may be brought together in the liquid state and other catalysts, *e.g.* glacial acetic acid, or anhydrous formic acid, may be employed. Or a mixture of dried chlorine and sulphur dioxide gases in approximately equimolecular proportions is brought in contact with charcoal. Bone charcoal or activated wood charcoal forms a most convenient catalyst for promoting the union of sulphur dioxide and chlorine to form sulphuryl chloride. Combination occurs instantaneously, and, provided that

the reaction vessel is cooled to 30°, the chloride is condensed and may be drained away as rapidly as it is formed. There seems to be no limit to the life of the catalyst (Sir William J. Pope, Rec. trav. chim. 1923, 42, 939–941; *cf.* T., 1920, 117, 1410; J. Chem. Soc. Abstr. 1923, 124, ii. 853). As a large quantity of heat is evolved during the reaction the vessel containing the charcoal should be cooled by water or ice (W. J. Pope, Eng. Pat. 122516, 1918; Roberts and Durrans, Eng. Pat. 124542). For the thermodynamics of this reaction, *see* Frantz, Zeitsch. Elektrochem. 1915, 21, 329. For the behaviour of sulphuryl chloride under the influence of light, *see* Le Blanc, Andrich and Kangro, Zeitsch. Elektrochem. 1919, 25, 229. Another method consists in boiling chlorosulphonic acid with about 1 p.c. of mercury or mercuric sulphate under a reflux condenser at about 75°–95° (Ruff, Ber. 1901, 34, 3509). For the precautions necessary, *see* Bert, Bull. Soc. Chem. 1922, 31, 1264. The product is rectified, and the portion boiling at 70°–72° collected separately. Sulphuryl chloride is a colourless liquid, b.p. 69.2°, sp.gr. 1.7045 at 0°. A small quantity of water converts it into chlorosulphonic acid, but a larger quantity decomposes it entirely into sulphuric and hydrochloric acids:



Added in small portions to ice-cold water, sulphuryl chloride forms a crystalline hydrate, stable at 0° (Baeyer and Villiger, Ber. 1901, 736).

On heating it splits up into SO₂ and Cl₂, the dissociation being complete at about 350°. On account of the ease with which it dissociates it acts as a powerful chlorinating agent, and has been patented for this purpose (for preparing the chlorides and anhydrides of organic acids):



For the action of sulphuryl chloride on metals and metalloids, *see* North and collaborators (*l.c.*).

Pyrosulphuryl chloride S₂O₅Cl₂ is produced by the action of sulphur trioxide on sulphur monochloride, phosphorus pentachloride, and other chlorine compounds. It is best prepared by acting on fuming sulphuric acid with carbon tetrachloride, a method first introduced by Schützenberger: $2\text{SO}_3 + \text{CCl}_4 = \text{COCl}_2 + \text{S}_2\text{O}_5\text{Cl}_2$. The carbon tetrachloride is placed in a flask fitted with a reflux condenser, and the oleum slowly added through a tap funnel. The flask is heated for some time after the evolution of phosgene has ceased, and the contents are then fractionated. The crude pyrosulphuryl chloride, thus obtained, is purified by the addition of fused sodium chloride and redistillation under reduced pressure, the sodium chloride combining with the chlorosulphonic acid present to form a salt, which remains behind in the distilling flask (*v.* Sanger and Riegel, Zeitsch. anorg. Chem. 1912, 76, 79).

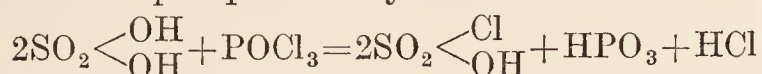
Pyrosulphuryl chloride is a colourless, fuming liquid, of sp.gr. 1.872 at 0°, m.p. –37.5°. It boils at about 153° at the ordinary pressure with slight decomposition, but may be distilled unchanged under 19 mm. pressure. It is slowly decomposed by water with formation of chloro-

sulphonic acid, which in turn yields hydrogen chloride and sulphuric acid as final products.

Fluorosulphonic acid $\text{SO}_2\text{<}^{\text{F}}_{\text{OH}}$ is formed by the direct union of sulphur trioxide with hydrogen fluoride at a low temperature. It is a colourless, mobile liquid, boiling at 162.6° , with slight decomposition (Thorpe and Kirman, Chem. Soc. Trans. 1892, 61, 921). For its salts, see Traube, Ber. 1913, 46, 2525.

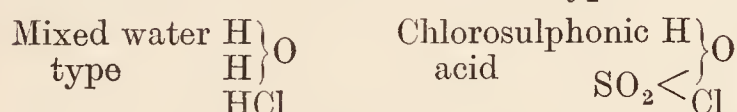
Sodium chloropyrosulphonate. See Traube, (Chem. Soc. Abstr. 1913, ii. 947).

Chlorosulphonic acid $\text{SO}_2\text{<}^{\text{Cl}}_{\text{OH}}$. This compound was first obtained by Williamson by the direct union of sulphur trioxide and hydrogen chloride, and by distilling a mixture of sulphuric acid and phosphorus oxychloride:

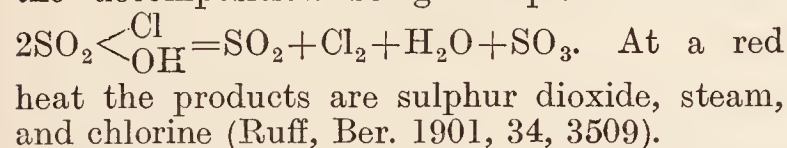


It is best prepared by the first-named reaction, by passing well-dried hydrogen chloride into fuming sulphuric acid until no further absorption takes place. The contents of the flask are then distilled in a current of dry hydrogen chloride, and the portion boiling at 145° – 160° collected separately. The product thus obtained may be further purified by redistillation, but if required perfectly pure must be crystallised several times at a low temperature. The melting-point of the pure acid is -80° .

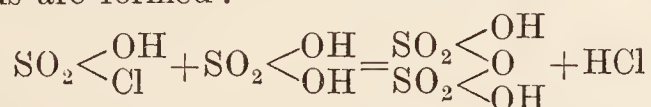
It had a special importance at the time of its discovery, as it was the first example of a substance to be referred to mixed types.



It is a colourless, fuming liquid of sp.gr. 1.784 at 0° , and boils with slight decomposition at 151° – 152° . Its vapour dissociates on heating, the decomposition being complete at 200° :



Chlorosulphonic acid is decomposed by water with explosive violence, forming hydrochloric and sulphuric acids, and when added to strong sulphuric acid, disulphuric acid and hydrochloric acids are formed:



With finely divided tellurium and selenium chlorosulphonic acid gives a cherry-red and a moss-green colour respectively. On standing for a considerable time the liquid becomes colourless.

Chlorosulphonic acid acts on many organic bodies with formation of sulpho-derivatives, and hence is often employed in the preparation of these compounds.

For an account of the literature on chlorosulphonic acid and pyrosulphuryl chloride, v. Sanger and Riegel, Proc. Amer. Acad. of Arts and Sciences, 1912, 47, 18.

Sulphur thiocyanate $\text{S}(\text{SCN})$ forms colourless pearly leaflets, unstable in air. When heated it rapidly darkens and suddenly decomposes, evolving an orange-coloured vapour. Prepared by the action of dry hydrogensulphide on a

solution of thiocyanogen in ether (Lecher and Wittwer, Ber. 1922, 55, [B], 1481).

Disulphur dithiocyanate $\text{S}_2(\text{SCN})_2$. Colourless crystals, m.p. -3.3° (corr.) to a yellow, odourless, viscous liquid, unstable, and decomposed on heating. Best prepared by the action of sulphur chloride upon mercuric thiocyanate (Lecher and Goebel, Ber. 1922, 55, [B], 1483).

OXIDES AND OXYACIDS OF SULPHUR.

Sulphur dioxide SO_2 . The ancients knew that when sulphur was burnt it evolved pungent fumes, and these fumes have long been used for fumigating purposes and for purifying cloth. It was formerly supposed that sulphuric acid was produced by burning sulphur in the air, but Stahl proved the fallacy of this assumption; the gas was then known as phlogisticated vitriolic acid, in accordance with the views of that time. Priestley, in 1775, first prepared the pure gas.

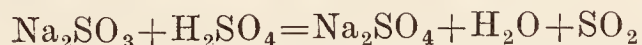
Occurrence.—Sulphur dioxide occurs among the gases issuing from volcanoes, and in a state of solution in the waters of certain volcanic springs. It also occurs to a small extent in the air of towns, being mainly derived from the pyrites contained in coal.

Preparation.—(1) By burning sulphur in air or oxygen. The sulphur ignites at a temperature of about 260° , and sulphur dioxide is obtained equal in volume to that of the oxygen consumed: $\text{S} + \text{O}_2 = \text{SO}_2$.

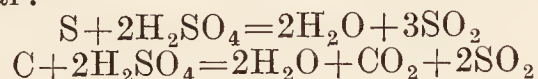
(2) By roasting pyrites. This method is mainly employed in the manufacture of sulphuric acid on the large scale.

(3) By heating a mixture of manganese dioxide and sulphur: $\text{MnO}_2 + \text{S}_2 = \text{MnS} + \text{SO}_2$.

(4) By the action of warm, dilute sulphuric acid on sulphites, as sodium sulphite:



(5) By heating sulphuric acid with certain deoxidising substances, such as sulphur and charcoal:



This latter reaction has been employed on the large scale in the manufacture of alkaline sulphites; the carbon dioxide simultaneously evolved is not detrimental, as it is almost insoluble in water containing sulphurous acid.

Properties.—Sulphur dioxide at ordinary temperatures is a colourless, irrespirable, incombustible gas, of sp.gr. 2.2639 (air=1). 1 litre of the gas at 0° and 760 mm. weighs 2.9266 grms. It may be collected by downward displacement like carbon dioxide, but if required quite free from air should be collected over mercury. Its viscosity is $\eta_{18} = 1.253 \times 10^{-4}$ C.G.S. units, and $\eta_{100} = 1.630 \times 10^{-4}$ (C. J. Smith, Phil. Mag. 1922, [vi.] 44, 508). It possesses the well-known smell of burning sulphur. Sulphur dioxide is very soluble in water, the solution being accompanied by a slight rise in temperature. At 0° water dissolves 79.79 times its volume of the gas, at 20° 39.37 volumes, and at 40° 18.77 volumes, prolonged ebullition being required to expel the last traces of the gas from the solution (Bunsen and Schoenfeld, Annalen, 95, 2). According to Freese (Chem. Zeit. 1920, 44, 294) 1 litre of water at 0° and 760 mm. pressure dissolves

228.29 grams of sulphur dioxide; at 10°, 162.09; at 20°, 112.90; at 25°, 94.08; at 30°, 78.67; and at 40°, 54.11 grams per litre. The solution of the gas has a strongly acid reaction, reddens blue litmus, and afterwards bleaches it, but the perfectly dry gas has not these properties. The gas is also soluble in alcohol. By cooling a saturated solution of the gas in water, hydrates containing 5, 8, 10, and 14 molecules of water have been obtained. They are colourless, crystalline bodies which melt at about 4°, and evolve SO₂ on exposure to air. For its solubility in benzene, toluene, nitrobenzene and o-nitrotoluene and acetic anhydride, see Lloyd, J. Phys. Chem. 1918, 22, 300; Moore, Morell, and Egloff, Met. and Chem. Eng. 1918, 18, 396. It is markedly soluble in sulphuric acid, in amount depending upon the strength of the acid and its temperature. 100 grams of 100 p.c. H₂SO₄ at 20° dissolves about 4.1 grams SO₂. The amount decreases with the strength of the acid until a minimum of 2.8 grams is reached at about 85–86 p.c. strength, after which it increases steadily to 5.2 grams at 55 p.c. strength (Miles and Fenton, Chem. Soc. Trans. 1920, 117, 59). Sulphur dioxide is poisonous; $\frac{1}{2500}$ part in air causes dyspnoea, and affects the eyes. It is absorbed by the blood, and transformed in the system into sulphuric acid. As little as 0.0005 p.c. can be detected by its smell, whilst in amounts above 0.05 p.c. the mixture is irrespirable. Air containing more than 0.003 p.c. is injurious to vegetation. Sulphur dioxide, both as a gas and in solution, is a powerful bleaching agent, and is used in bleaching those materials which would be injured by chlorine; this property was known to Paracelsus. The bleaching action of sulphur dioxide is a reducing one, whilst that of chlorine is an oxidising one; thus sulphur dioxide in the presence of moisture is oxidised to sulphuric acid, the liberated hydrogen reducing the colouring matter to a colourless compound. The colouring matters are probably in many cases not destroyed by the acid, but reduced to colourless leuco compounds, for in time the original colour often reappears, as in the case of bleached straw and flannel, which become yellow with age. Sulphur dioxide and hydrogen sulphide mutually decompose one another in the presence of moisture, with decomposition of sulphur and formation of water and polythionic acids (Wackenroder's solution). When sulphur dioxide and oxygen or air are passed over heated spongy platinum, the two gases combine to form sulphur trioxide. The platinum can be replaced by other substances, and the sulphur trioxide so produced is now used commercially in the manufacture of sulphuric acid (see under SULPHURIC ACID). With ammonia gas sulphur dioxide forms various compounds, according as the one or other gas is in excess. With an excess of SO₂, aminosulphinic acid NH₂·SO₂H is always formed, but with excess of ammonia either white NH₂·SO₂NH₄ or red NH₄N(SO₂NH₄)₂ are obtained (see Divers and Ogawa, Chem. Soc. Trans. 1901, 79, 1102; Ephraim and Pistrowski, Ber. 1911, 44, 379). Many metals are attacked when heated in the gas; potassium burns with formation of potassium thiosulphate and sulphite, and tin and finely divided iron are changed partly into sulphides and partly into oxides.

When the gas is passed over metallic peroxides, e.g. lead peroxide, sulphates are formed, often with considerable evolution of heat. For observations on the action of sulphur dioxide on various metallic oxides, see Hammick, Chem. Soc. Trans. 1917, 111, 379. Sulphur dioxide is a strong reducing agent, being readily converted into sulphuric acid by addition of oxygen; the halogens are converted by it into the halogen acids, and solutions of the noble metals are reduced with precipitation of the metal. Under certain conditions sulphur dioxide behaves as an oxidising agent. Stannous and titanous chlorides are oxidised in warm strongly acid solution to stannic and titanic chlorides respectively, the sulphur dioxide being converted into hydrogen sulphide and free sulphur (cf. Durrant, Chem. Soc. Trans. 1915, 107, 622; Wardlaw and Clews, *ibid.* 1920, 1093; Woodlaw, Carter and Clews, *ibid.* 1920, 1241). At temperatures below 2200° absolute sulphur dioxide experiences no appreciable dissociation (Wartenberg, Zeitsch. anorg. Chem. 1908, 56, 320). Decomposition takes place when electric sparks are passed through the gas, but the decomposition is only complete when the sulphur trioxide is removed as soon as formed by absorption with sulphuric acid. Tyndall has shown that the gas is also decomposed by passing a beam of sunlight through a long tube filled with the gas, when a white cloud is formed, consisting of sulphur trioxide and sulphur.

The final result of the decomposition of sulphur dioxide gas under the action of light from a Uviol mercury vapour lamp is represented by the equation $3\text{SO}_2 = 2\text{SO}_3 + \text{S}$. The wave-length chiefly responsible for such decomposition is 313μμ, the shorter wave-lengths contributing very little. This wave-length lies within the first absorption band of sulphur dioxide (at 600 mm. pressure), but does not coincide with the head of the band, which is at 296.1μμ. The actual wave-length producing maximum decomposition depends upon the intensity distribution of the emission spectrum of the source of radiation. In the radiation emitted by the Uviol lamp the longest wave-length capable of decomposing sulphur dioxide gas is the 313μμ line itself, but it is concluded that any wave-length within the absorption band of the substance is capable of causing decomposition provided the intensity is sufficiently great (R. A. Hill, Trans. Faraday Soc. April, 1924; J. Soc. Chem. Ind. 1924, 43 B, 418).

Sulphur dioxide acts on calcium sulphide at temperatures below 1000° to give the sulphate and sulphur, but the reaction is soon brought to a standstill owing to the formation of a protective layer of sulphate on the pieces of sulphide. By working at temperatures above 1000° this can be avoided, as the reaction products are lime and sulphur. The low temperature reaction can, however, be accelerated by the addition of triferrie tetroxide, which acts as a catalyst. Zinc blende reacts with sulphur dioxide to give the oxide and sulphur, but here again the reaction velocity rapidly diminishes owing to the formation of a protective layer, in this case of basic sulphide. Both sulphides of iron react with sulphur dioxide to give triferrie tetroxide and sulphur. The reaction is rapid

and complete, being catalytically accelerated by the oxide (Lothar Wöhler, F. Martin, and E. Schmidt, *Zeitsch. anorg. Chem.* 1923, 127, 273-294; *J. Chem. Soc. Abstr.* 1923, 124, ii. 852).

The composition of sulphur dioxide is ascertained by burning sulphur in a flask of oxygen inverted over mercury. The sulphur is placed in a cup inside the flask, and is so arranged that the sparks from an induction coil, on passing between wire terminals, come in contact with and ignite the sulphur. The volumes of oxygen before the combustion and of sulphur dioxide after combustion, are found to be the same.

Langmuir considers that in the molecule of SO_2 each oxygen atom, by holding electrons in common with other atoms, has got the configuration of neon, with 10 electrons round the nucleus instead of 8; and sulphur, like argon, has 18 instead of 16, the number of extra-nuclear electrons in the uncombined atom. He represents the molecule as $\text{O}=\text{S}-\text{O}$, the single bond meaning that two electrons are shared and the double bond that four are shared. A. O. Rankine and G. J. Smith consider this

arrangement, and also the arrangement $\text{S} \begin{smallmatrix} \diagup \text{O} \\ \diagdown \text{O} \end{smallmatrix}$ in which six electrons are also shared between the atoms. Dimensionally it may be assumed that the molecule has the properties of a particular arrangement of two neon atoms and one argon atom, the radii of the collision spheres of which, as determined by viscosity measurements, are 1.44 Å and 1.15 Å. W. L. Bragg's crystal measurements lead to similar values for the radii of the outer electron shells. The mean area which any particular model presents in collision for all orientations can be calculated; and when this is done for the second of the above arrangements the value $0.99 \times 10^{-15} \text{ cm.}^2$ is found for the collision area. The value obtained from viscosity measurements is $0.94 \times 10^{-15} \text{ cm.}^2$, which is sufficiently near to that of the model to enable the difference to be attributed to experimental errors and inexactitudes in the assumptions. The arrangement $\text{O}=\text{S}-\text{O}$ is indeterminate, as the two oxygen atoms need not be at opposite ends of a diameter of the sulphur. It is shown that the mean area will always be greater than 0.99×10^{-15} , which was the value obtained for the second arrangement; and it is concluded that the second arrangement is the correct one (A. O. Rankine and C. J. Smith, *Phys. Soc. Proc.* 35, 33-37; *Science Abstracts*, 1923, 26, 251).

Liquid sulphur dioxide.—Sulphur dioxide is condensible to a liquid at the temperature obtainable by a mixture of ice and salt, or by a pressure of about $2\frac{1}{2}$ atmospheres at ordinary temperatures. Its critical temperature is 157.15° , and critical pressure 77.65 atmospheres; its critical density is 0.52. The liquid acid is a colourless, mobile fluid, of sp.gr. 1.4338. It boils at -10.2° , and on being cooled solidifies to a white mass melting at -72.7° . The liquid oxide dissolves many salts and organic bodies and acts as a dissociating medium when used as a solvent in cryoscopic molecular weight determinations. It is miscible with many organic liquids, such as carbon disulphide and chloroform. With potassium iodide at tem-

peratures below 0° , it forms a compound $\text{KI}(\text{SO}_2)_4$, and the formation of similar compounds has also been observed in the case of other salts. If free from water it has no action on iron, hence the liquid oxide can be transported in wrought-iron cylinders. Owing to the rapid increase in the pressure of the SO_2 with rise of temperature, these must only be seven-eighths filled. The pressure in atmospheres of SO_2 at various temperatures is given below—

Pressure	Temperature	Pressure	Temperature
0	-10°	3.51	30°
0.53	0°	5.15	40°
1.26	$+10^\circ$	7.18	50°
2.24	20°		

The vapour pressures of liquid sulphur dioxide between -11° and -64.5° can be represented by the equation:

$$\log p = -1448.01/T + 8.425$$

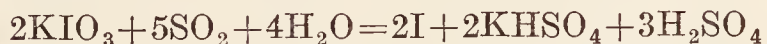
(Burrell and Robertson, *J. Amer. Chem. Soc.* 1915, 37, 2691).

Mund (*Bull. Acad. roy. Belg.* 1919, [v.] 5, 529) has determined by the static method the vapour pressures of sulphur dioxide at temperatures between -42° and 0° . The vapour pressure at 0° was found to be 1163.98 mm. or 1.53 atmos.

The liquid oxide is now sold for laboratory use in glass syphons, fitted with a screw valve, so arranged that either the liquid oxide or the gas may be obtained as desired, the current of gas being capable of adjustment to any desired speed by regulating the screw. A single syphon will evolve 500 litres of gas. It is transported in steel cylinders holding up to 2 cwts., or in tank waggons containing as much as 10 tons. Sulphur dioxide can be employed in the artificial production of low temperatures; a mixture of 3 p.c. CO_2 and 97 p.c. SO_2 was employed by Pictet for this purpose. This mixture boils at -19° . The low temperature of -140° is obtained by the evaporation of a solution of solid carbon dioxide in liquid sulphur dioxide.

For a method of making liquid sulphur dioxide as used in the Sarandi Works at Buenos Ayres, see Paoli, *Giorn. Chim. Appl.* 1922, 4, 449; *J. Soc. Chem. Ind.* 1922, 41, 896 A).

Detection of sulphur dioxide.—For this purpose paper steeped in a solution of potassium iodate and starch is brought into the gas under examination, when a blue colour is at once produced if only traces of sulphur dioxide are present, iodide of starch being formed:



When the sulphur dioxide is in excess the blue paper is again bleached, hydriodic acid being formed: $2\text{I} + \text{SO}_2 + 2\text{H}_2\text{O} = 2\text{HI} + \text{H}_2\text{SO}_4$.

This latter reaction is utilised in determining the amount of sulphur dioxide present in a solution. The solution under examination is placed in a burette and run into standard iodine solution containing a little starch paste, until the blue colour of the liquid disappears. The reverse process—running the iodine into the SO_2 solution—is not applicable, as in this case the action proceeds partly according to the following equation: $\text{SO}_2 + 4\text{HI} = 4\text{I} + 2\text{H}_2\text{O} + \text{S}$, the hydriodic acid formed reducing a part of the sulphurous acid to free sulphur.

Commercial manufacture of sulphur dioxide.—The action of sulphuric acid on sulphur and charcoal is used only in the production of an aqueous solution of the gas. Liquid sulphur dioxide was first produced on a large scale by Pictet, who prepared the gas from sulphur

and sulphuric acid in an iron retort lined with firebricks, cooled it to -10° , when all the moisture separated out in the form of hydrates, and compressed the residual dry gas with a pump. This process, however, is now superseded by that of Hänisch and Schröder. By

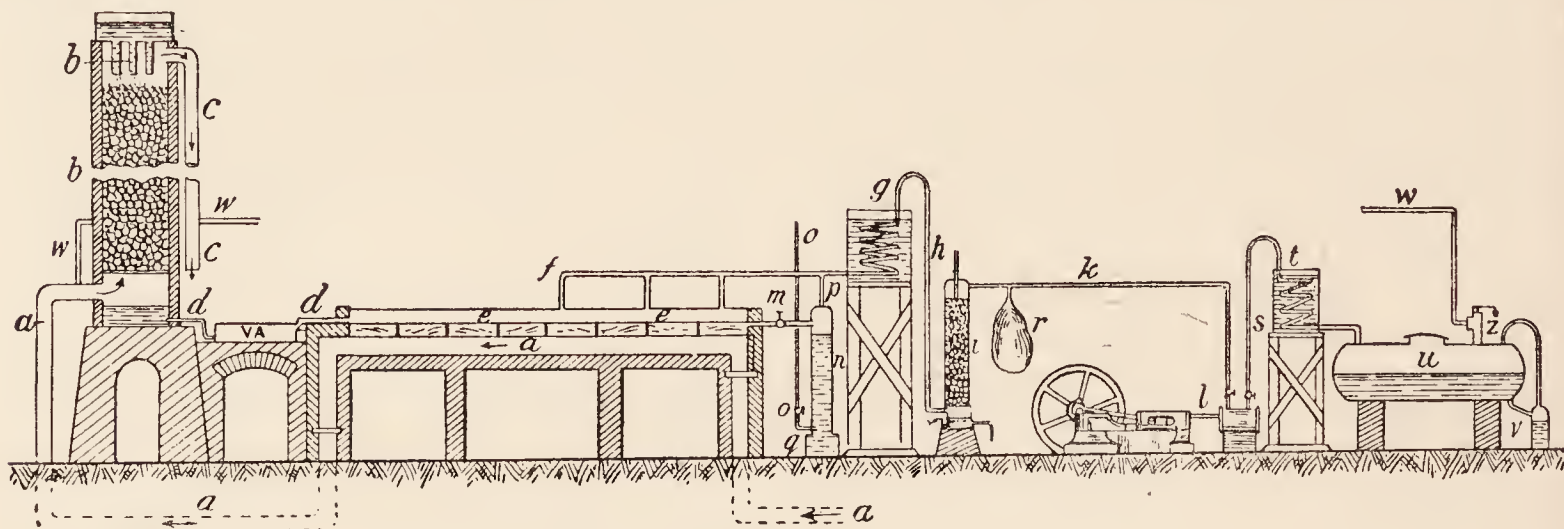


FIG. 5.

means of this process, liquid SO_2 can be manufactured in a pure condition directly from the gases obtained by roasting zinc blende; these gases contain about 6–7 p.c. of SO_2 . The method adopted is as follows, Fig. 5 being a sketch of the apparatus employed.

The gases from the roasting furnaces pass through the channel *a* under the leaden pans *e, e*, and in so doing part with their heat to these. They then enter the tower *b*, packed with coke or firebrick, down which a stream of cold water trickles. Practically complete absorption of the sulphur dioxide takes place, the residual air escaping through the pipe *c*. The aqueous solution of sulphur dioxide which collects at the bottom of the tower runs through the preliminary heater *va*, composed of thin plates of lead around which hot waste liquors from a subsequent stage of the process circulate. The temperature of the issuing liquid is thus raised to about 85° . The liquid next runs over the lead pans *e, e*, and its temperature is raised to boiling by the heat of the flue gases passing underneath. The expelled sulphur dioxide passes through the pipe *f* to the worm *g*, where it is cooled and most of the accompanying moisture deposited. The last traces of moisture are removed by passage through the tower *i*, packed with coke, down which concentrated sulphuric acid trickles. The perfectly dry gas passes on through *k* (*r* is a taffeta bag to regulate the pressure), into the pump *l*, which is made of bronze. The gas is forced through *s* into *t*, where it is liquefied (for which a pressure of $2\text{--}3\frac{1}{2}$ atmospheres is necessary, according to the season of the year). The liquefied gas then passes into the wrought-iron vessel *u*, whence it is drawn off as required, into small iron cylinders *v*. In order to recover the sulphur dioxide which remains in the liquid running away from the pans *e, e*, it is run into the small tower *n*, packed with lead wire. Steam is blown in through the pipe *o*, the remaining sulphur dioxide is completely expelled, and passes along with some steam into *g*, and the boiling water which collects at the bottom of *n* is used to circulate round the plates of the heating apparatus *va*.

The pans *e, e*, are frequently omitted in

practice, and the preliminary heater *va* connected direct with the tower *n*. Instead of a simple worm, a tower (see Fig. 6) may be used for depriving the sulphur dioxide of the greater part of its moisture. The upper part of this tower is packed with coke, the lower half filled with perforated stoneware plates; the moist gas enters at the bottom, whilst a stream of water is run in at the top. By carefully adjusting the proportions of water and gas, boiling water collects at the bottom of the tower, whilst a steady stream of practically dry sulphur dioxide escapes through the tube *d*.

For this process to be successfully worked a minimum percentage of 4 p.c. sulphur dioxide must be present in the entering gas, otherwise too much water is required for the complete condensation of the sulphur dioxide.

The liquid sulphur dioxide sold commercially has frequently a purity of 99.8 p.c.

Uses.—Sulphur dioxide is largely employed in the arts and manufactures.

Its principal use is in the manufacture of sulphuric acid, enormous quantities of the gas being produced for this purpose, principally from pyrites.

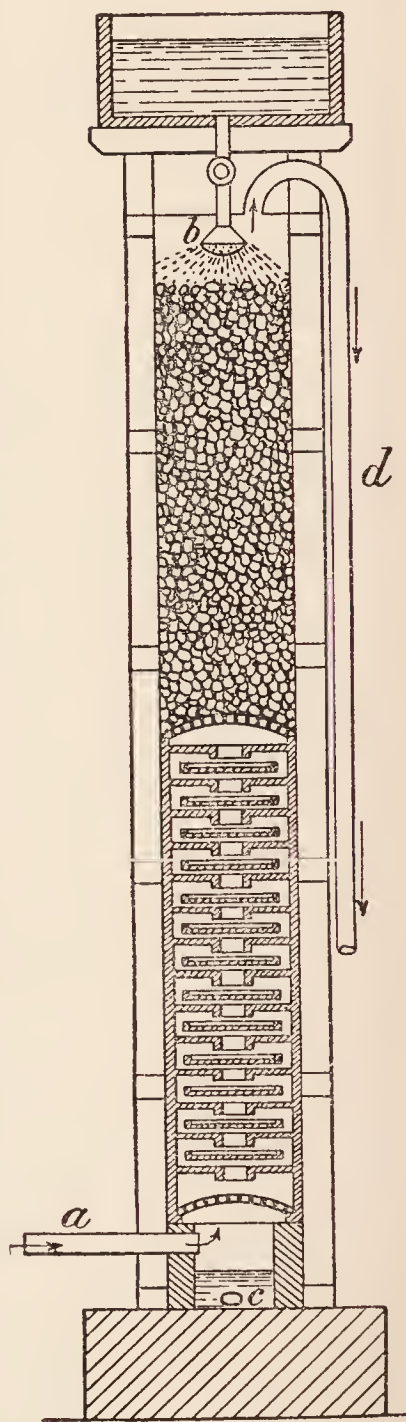


FIG. 6.

The liquid acid was formerly largely used in the paper industry in the manufacture of wood pulp, but has now been superseded to a great extent by sulphur dioxide prepared by burning sulphur or roasting pyrites. In this process the fir or pinewood is deprived of the bark, cut up into small pieces, and boiled in large lead-lined boilers with a solution of calcium sulphite in excess of sulphurous acid until all incrusting matter is dissolved, and the cellulose can easily be separated from the residue by washing and beating. Sulphur dioxide is also employed to remove the last traces of chlorine after bleaching the pulp: $\text{SO}_2 + \text{Cl}_2 + 2\text{H}_2\text{O} = \text{H}_2\text{SO}_4 + 2\text{HCl}$. It is also used in the refining of sugar, to decolorise the crude sugar juice; it does not invert the sugar, unless exposed to the air for a long time, and has a slight preservative action. It has been employed in tanning to soften dry hides and skins in the bath or 'soak,' which consists of a solution of sulphur dioxide, and in the 'puring' operation for the purpose of curtailing or dispensing with the use of animal excrement. Sulphur dioxide is a powerful antiseptic and has been successfully employed in preserving meat and stopping fermentation, fumigating clothes, and disinfecting the air of rooms. Instead of burning sulphur for disinfecting purposes, the sulphur dioxide can conveniently be obtained from the liquid oxide.

Sulphur dioxide is used in the extraction of alum from shale in a process worked at Ampsin near Luttich; as a fire extinguisher; and in the bleaching of wool, silk, feathers, sponges, starch, and many other substances.

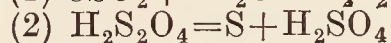
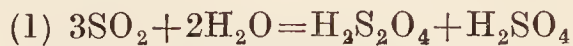
The materials to be bleached may be treated either with the gas or the solution, the latter being less effective. The goods, after washing and wringing, are brought, while still damp, into a closed chamber, and covered with a thick cloth. They are then exposed to the action of sulphur dioxide for 12–24 hours according to the whiteness required. They are then washed in lukewarm, dilute hydrochloric acid to remove particles of adhering sulphur deposited on them. For bleaching loose wool a solution of sodium bisulphite is preferably used, the substance being afterwards passed through lukewarm, dilute hydrochloric acid, whereby sulphur dioxide is evolved in the nascent condition and bleaches the wool (Dingl. poly. J. 245, 183).

Sulphurous acid has been used to a considerable extent for the purpose of giving to old barley the fine yellow colour of the new grain. Such treatment is injurious to the germinating power, and may be detected by steeping the barley in hot water for a quarter of an hour, then adding zinc and hydrochloric acid to the aqueous extract, the presence of sulphur being indicated by the evolution of hydrogen sulphide (Eckenroth).

Sulphur dioxide has been employed in the treatment of cutaneous diseases, the patient sitting in a box provided with an aperture at the top, through which his head passes, while a wet cloth around his neck prevents the escape of gas from within. The box is over a small fireplace in which sulphur is burned, so that the patient sits in an atmosphere of sulphur dioxide.

The liquid oxide is employed principally as a source of the gas, but is also used directly to some extent in the manufacture of artificial ice, and the extraction of certain fats and oils.

Sulphurous acid. This acid is known only in solution, which is prepared by saturating water with sulphur dioxide. The resulting liquid smells and tastes of the gas, and has a strongly acid reaction. In contact with air the smell gradually disappears, oxygen being absorbed, sulphur and sulphuric acid formed. This production of sulphur and sulphuric acid takes place in two stages, the first of which is, at low temperatures, the formation of hypsulphurous acid:

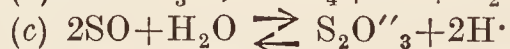


(Jungfleisch and Brund, Compt. rend. 1913, 156, 1719). The acid is dibasic, and forms two series of salts known as sulphites, the two types $\text{R}'\text{HSO}_3$ and $\text{R}''_2\text{SO}_3$ being termed acid and normal sulphites respectively. The normal sulphites of the alkalis are easily soluble in water, while those of the other metals are almost, or quite, insoluble. These latter dissolve, however, in aqueous sulphurous acid with formation of the acid sulphites, but the solution thus obtained is again decomposed on evaporation with evolution of SO_2 , and formation of the normal salt. In addition to the two series of sulphites mentioned above, a third series is known, termed metabisulphites, of the formula $\text{R}''_2\text{S}_2\text{O}_5$. Only the alkali salts of this last class have been prepared.

Concentrated solutions of sulphites are oxidised slowly at ordinary temperatures by air, and in some cases the sulphate formed catalytically accelerates the change. The sulphites, bisulphites, and metabisulphites undergo auto-reduction when heated to 150° – 200° with production of sulphur, a sulphate, and thio-sulphate (Geuther, Annalen, 1884, 224, 218; Divers, Chem. Soc. Trans. 1885, 47, 205). According to Bennett (Chem. Soc. Trans. 1922, 121, 1794) sulphurous acid, liberated in solution from its salts at 100° – 120° , or lower, may undergo instantaneous autoreduction with production of hydrogen sulphide: $4\text{H}_2\text{SO}_3 = \text{H}_2\text{S} + 3\text{H}_2\text{SO}_4$. It represents a possible intermediate stage in the liberation of free sulphur.

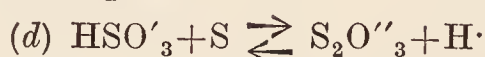
Sulphurous acid reacts with hydrogen sulphide in aqueous solution forming eventually sulphur and water, but the course of the change is accompanied by a number of reversible reactions, depending on the relative proportions of the reacting gases and on the order of their addition, and involves the formation of polythionic acids (Heinze, J. pr. Chem. 1919, [ii.] 99, 109).

The spontaneous decomposition of sulphurous acid, forming sulphuric acid and sulphur, proceeds extremely slowly, requiring at 100° several days and at 150° about two days for completion. The change is autocatalytic, being accelerated by the sulphur and retarded by hydrogen ions, the latter effect masks the former as the change proceeds. Dilute solutions decompose more quickly and completely than concentrated solutions, whilst in acid solutions the decomposition is inhibited, being completely suppressed in 2N-hydrochloric acid solution. The first stages in the decomposition are probably

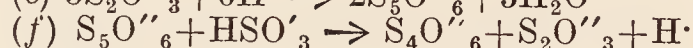
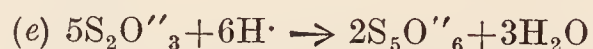


(b) being extremely slow. The positive catalytic

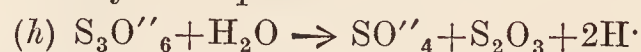
action of sulphur is probably due to the formation of thiosulphate



which is very rapid in comparison with (b) and (c), and gives rise to penta-, tetra-, and tri-thionic acids, thus



and finally to sulphuric acid

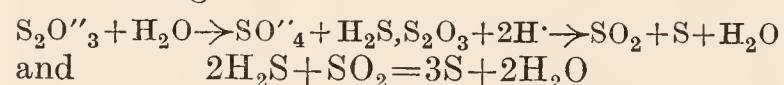


all these changes, (e) to (h), proceeding very rapidly in comparison with (b); the intermediate polythionic acids increase rapidly in solution at the beginning. The thiosulphuric acid formed is, however, transformed back to sulphurous acid by hydrogen ions



which reaction prevents the changes (d) to (h) and brings the decomposition to a halt.

The strong positive catalytic effect of hydriodic acid on the decomposition is ascribed to the formation of complex ions. The decomposition of the metal hydrogen sulphites is different from that of the acid itself in that until the decomposition is far advanced the concentration of hydrogen ions remains low, being that of a hydrogen sulphite-sulphurous acid solution; the change is therefore very strongly positively autocatalytic, and is greatly hastened by addition of sulphur or polythionates. If sulphur dioxide is allowed to escape from the solution, as by boiling a strong sodium hydrogen sulphite solution in an open vessel, polythionic acids are not formed, the mechanism following (b) and (c) above being



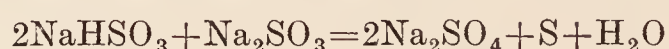
Selenium and selenious acid act as powerful catalysts, forming the selenosulphuric-ion SeSO''_3 in the solution. Potassium selenosulphate and selenodithionate have been prepared in the pure state, and indications of the existence of selenium analogues of the polythionic acids obtained. The mechanism of the series of changes (e) to (h) when selenium dioxide is substituted for sulphur dioxide has been examined. Tellurium when free from selenium has no catalytic activity with regard to the decomposition of hydrogen sulphites (F. Foerster, F. Lange, O. Drossbach and W. Seidel, *Zeitsch. anorg. Chem.* 1923, 128, 245; *Chem. Soc. Abstr.* 1923, 124, ii. 853).

The normal sulphites have no odour, and those which dissolve in water possess a sharp taste. They are easily detected by the addition of sulphuric acid when they evolve the pungent-smelling SO_2 . Their neutral solutions give a white precipitate with barium chloride, which is easily soluble in dilute hydrochloric acid; on adding nitric acid to this solution and warming, a precipitate of barium sulphate is obtained.

The existence of isomeric double sulphites, which are theoretically possible owing to the unsymmetrical formula of sulphurous acid $\text{H}\cdot\text{SO}_2\cdot\text{OH}$, has been announced by Schwicker (Ber. 22, 1728), who describes two different salts, to which he assigns the formulæ $\text{Na}\cdot\text{SO}_2\cdot\text{OK}$

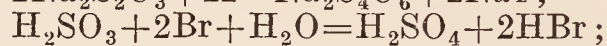
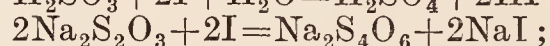
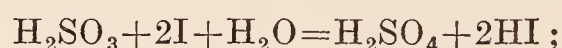
and $\text{K}\cdot\text{SO}_2\cdot\text{ONa}$. Subsequent observers have, however, failed to obtain these compounds, and their existence is not satisfactorily established, see Godby, *Chem. Soc. Proc.* 1907, 241; Arbusoff, *Chem. Soc. Abstr.* 1909, ii. 573.

When a mixture of a sulphite and a hydrogen sulphite is heated under pressure sulphur and a sulphate are formed thus:



(Farbenfabr. vorm. Fried. Bayer and Co. D.R.P. 265167).

The difficulties of the titration of sulphurous acid by iodine are due to atmospheric oxidation. For the analysis of a mixture of a sulphite and a thiosulphate, a method based on titration with iodine and with bromide-bromate may be employed. The reactions are as follows:—



From the results the amount of each acid in the mixture can be calculated (C. Mayr and J. Peyfuss, *Zeitsch. anorg. Chem.* 1923, 127, 123–136; *J. Soc. Chem. Ind.* 1923, 42, 1128 A).

Determination of sulphur dioxide in sodium bisulphite solution.—According to L. Debucquet (*J. Pharm. Chim.* 1924, 29, 66), 1 c.c. of the sample is diluted with 20 c.c. of water, 25 c.c. of 5 p.c. mercuric chloride solution are added, and the mixture is titrated with *N*/10 sodium hydroxide solution, using methyl orange as indicator. Each c.c. of *N*/10 alkali solution = 0.0064 gm. SO_2 (*J. Soc. Chem. Ind.* 1924, 43 B, 253).

Sulphur sesquioxide. Buchholz was the first to observe the formation of a blue solution when flowers of sulphur were dissolved in Nordhausen sulphuric acid. Vogel found that the same colour was produced with S and SO_3 , but Weber was the first to show that it was due to the formation of a new oxide of sulphur (*Pogg. Ann.* 1875, 156, 531).

Sulphur sesquioxide is obtained by dissolving flowers of sulphur in an excess of sulphur trioxide cooled to 15°, when it forms bluish-green crusts resembling malachite. It may be isolated by pouring off as much as possible of the excess of SO_3 , and distilling off the rest at a temperature of about 38°, the sesquioxide remaining behind. It forms a crystalline, blue-green mass, which easily decomposes, especially on heating, into sulphur and sulphur dioxide. In moist air it absorbs water, giving a brown liquid, which soon decomposes with precipitation of sulphur. It is soluble in fuming sulphuric acid, producing a blue solution, which is comparatively stable, and may be kept for a considerable time in a sealed tube, but eventually decomposes, giving a brown solution with evolution of sulphur dioxide and precipitation of sulphur. This solution is used in the manufacture of certain colours (sulphur colours), such as thiopyronine.

Sulphur trioxide SO_3 .—Sulphur trioxide was known to the alchemists under the name of 'philosophical salt,' and a method for its preparation by the distillation of ferric sulphate is mentioned by Lemery in 1675. Its relations

to oil of vitriol were first recognised by Scheele and Guyton de Morveau in 1786.

Preparation.—Sulphur trioxide may be prepared by carefully heating fuming sulphuric acid in a retort, and collecting the distillate in a well-cooled receiver. It is also formed when concentrated sulphuric acid is distilled with an excess of phosphorus pentoxide, and by the dry distillation of many metallic sulphates, especially ferric sulphate. Sulphur dioxide unites directly with oxygen to form sulphur trioxide in the presence of certain substances such as platinised asbestos and ferric oxide, which act as catalysts, and this reaction is now employed on the large scale in the contact process for manufacturing sulphuric acid (*q.v.*). Sulphur trioxide is also produced to some extent when sulphur dioxide is decomposed by heat or by passing electric sparks through it, as well as during the combustion of sulphur and the roasting of metallic sulphides. If pure sulphur trioxide be required, the product obtained by any of the above processes must first be redistilled several times, and finally purified by repeatedly heating it until it has almost entirely melted and then pouring off the liquid from the portions still remaining solid. The sulphur trioxide may be regarded as pure when the whole mass melts easily and completely on gentle warming.

Properties.—Sulphur trioxide exists in two modifications termed α and β respectively. The two substances have different physical properties but resemble one another in their chemical behaviour.

α -Sulphur trioxide forms long colourless needles of sp.gr. 1.944 at 11° (Schenck, *Annalen*, 1901, 316, 1), which melt at 14.8° (Rebs), 16.79° (Lichty), 16.85 ± 0.02 (Berthoud, *Helv. Chim. Acta*, 1922, 5, 513), and at temperatures below 25° gradually pass over into the β modification. The liquid boils at 44.88° (Lichty, *Amer. Chem. J.* 1912, 34, 1440), 44.52° (Berthoud). Critical temp. 218.3°, critical pressure 83.8 atms., critical density 0.633; mol. heat of vaporisation 10,300 cal.; van der Waals' constants

$$a=0.01629, \quad b=0.002684,$$

and its molecular weight corresponds with the formula SO_3 (Oddo, *Gazz. chim. ital.* 1901, 31, (2), 158).

Sulphur trioxide dried for twenty years had the m.p. 61.5° for the α -form and changed on melting to a β -form of m.p. 15.5°, the corresponding temperatures for material not specially dried being 50° and 14.4° (H. B. Baker, *l.c.*).

β -Sulphur trioxide crystallises in colourless needles of sp.gr. 1.97 at 20°, which resemble asbestos in appearance. On heating, it volatilises at about 50° without previous fusion, and is converted into the α modification by distillation. According to Oddo, the molecular weight of the β compound corresponds with the formula S_2O_6 (see, however, Lichty, *l.c.*). The β modification is chemically rather less active than the α modification.

According to Berthoud (*l.c.*) it is probably a hydrated form, owing its formation to the presence of water, but cannot contain more than 1 mol. of water per 1000 mols. of sulphur trioxide.

According to M. Le Blanc and C. Rühle (*Ber. Sachs. Ges. Wiss., Math-phys. K. I.* 1922, 74, Vol. VI.—T.

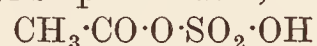
106–144; *Chem. Zentr.* 1923, 94, iv. 522–523), an investigation of the formation of sulphur trioxide from sulphur dioxide and oxygen at 150°, under reduced pressure, in presence of light, gave no constant results. The gaseous sulphur trioxide first formed was gradually converted into a solid modification. Further, if solid sulphur trioxide is warmed to 17° part of it melts, but with repetition the proportion remaining solid above 17° continually increases. Four modifications, a , b , c , d , having vapour pressures increasing in the order given, are described; a has m.p. 95°–100°, and is obtained by condensation of the vapour in the form of needles or delicate membranes; b , m.p. 31°, is formed as a tough white mass by condensation at 0°, the generating vessel being at 6°–7°; c , which passes readily into a and b , and d both melt at 16.8°, but differ in appearance and in behaviour on cooling. Owing to the general instability of these modifications no separate vapour pressure curves could be determined (*J. Soc. Chem. Ind.* 1923, 42, 972 A).

The β -modification of sulphur trioxide is not a simple polymeric form of the α -variety, but probably an indefinite hydration compound. Sulphur trioxide boils at 44.52°, melts at 16.85 ± 0.02 °, and has critical density 0.663, critical temperature 218.3°, and critical pressure 83.8 atms. The molecule is double (S_2O_6) at temperatures between 29.47° and 78° (A. Berthoud, *J. Phys. Chem.* 1923, 20, 77–86; *J. Soc. Chem. Ind.* 1923, 42, 449 A).

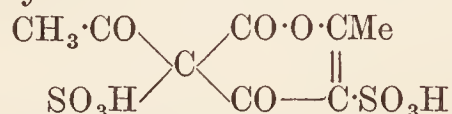
Perfectly dry sulphur trioxide shows no acid reaction and is not corrosive. On heating, it is decomposed into sulphur dioxide and oxygen, but a temperature of 1300° is required for the reaction to be complete. On exposure to air it absorbs moisture rapidly, emitting dense white fumes, whilst it combines with water with explosive violence, producing sulphuric acid. Owing to this avidity for water, sulphur trioxide chars many organic substances.

Sulphur trioxide forms stable compounds with many substances, such as iodine, with which it gives rise to the compounds $\text{I}_2(\text{SO}_3)_4$ and $\text{I}_2(\text{SO}_3)_2$. With tellurium it forms TeSO_3 , a solid possessing a characteristic red colour. Compounds of sulphur trioxide with the oxides of arsenic and nitrogen are also known.

Sulphur trioxide acts on acetic acid at 0° forming acetyl-sulphuric acid,



It reacts with sodium acetate to form sodium acetyl-sulphate. This salt when heated decomposes, giving sodium pyrosulphate and acetic anhydride, but when heated with acetic acid gives acetic anhydride and sodium hydrogen sulphate, a reaction which is reversible. When heated at 70°, acetyl-sulphuric acid is converted into sulphoacetic acid, which is readily acetylated by acetyl-sulphuric acid forming acetyl-sulphoacetic acid which readily condenses to form disulphodehydroacetic acid



Acetyl-sulphuric acid is a vigorous acetylating agent, but in some cases it acts as a sulphonating agent (van Peski, *Rec. trav. chim.* 1921, 40, 103; *Chem. Soc. Report* 1921, 63).

Uses.—Sulphur trioxide is manufactured on the large scale for use in the preparation of artificial dyestuffs and explosives, in which it is employed as a sulphonating and oxidising agent. It is formed as an intermediate body in the contact process for manufacturing sulphuric acid (*q.v.*).

Hyposulphurous acid (*Hydrosulphurous acid*). Berthollet, in 1789, found that iron dissolved in an aqueous solution of sulphur dioxide without evolution of hydrogen, and Fourcroy and Vauquelin discovered in 1798 that tin and zinc behave similarly. Schönbein studied the reaction between zinc and sulphurous acid, and showed that the solution thus obtained possessed strong reducing properties, and that it contained the salt of a sulphur acid containing less oxygen than sulphurous acid, but the true nature of the reaction was first traced by Schützenberger, to whom the credit of the discovery of hyposulphurous acid is due (Compt. rend. 1869, 69, 196).

Preparation.—The zinc salt of the acid is produced when zinc is dissolved in a strong solution of sulphurous acid, and the solution so obtained was mistaken by Schützenberger for the free acid: $\text{Zn} + 2\text{SO}_2 = \text{ZnS}_2\text{O}_4$.

A better method for preparing hyposulphites is that of Bernsthen and Balzen (Ber. 1900, 33, 126). A concentrated solution of sodium bisulphite is shaken with zinc-dust, or electrolytic zinc sponge (Fr. Pat. 467443 of 1914), and sulphur dioxide is passed into the liquid



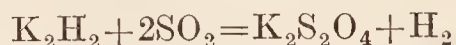
Milk of lime is then added until the zinc is precipitated, the solution filtered, and the filtrate saturated with sodium chloride. On cooling the liquid, crystals of $\text{Na}_2\text{S}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ separate out.

Sodium hyposulphite is formed in the electrolytic reduction of sodium bisulphite, but it is difficult to prevent the reduction from proceeding further, with the consequent formation of thio-sulphate: $\text{Na}_2\text{S}_2\text{O}_4 + \text{H}_2 = \text{Na}_2\text{S}_2\text{O}_3 + \text{H}_2\text{O}$. Cf. Jellinek, Zeitsch. anorg. Chem. 1911, 70–93.

By using suitable precautions, solutions containing 30–40 grms. of hyposulphite per litre can be obtained (Frank, Zeitsch. Elektrochem. 1904, 10, 460). If the bisulphite be electrolysed in the presence of indigo, indigo-white is produced, the hyposulphite first formed acting on the indigo, and this process is now employed commercially.

According to D.R.PP. 276058, 276059, 1912, dilute sodium bisulphite solution is electrolysed in the cathode compartment. A neutral salt, such as chloride or sulphate, but not a sulphite, may be added with good results, temp. 0° – 5° . During electrolysis sulphurous acid is added to the bisulphite solution. The process is made continuous by circulating the bisulphite from a reservoir through the electrolytic vessels and back again. When the liquor becomes sufficiently concentrated, sodium hyposulphite (hydrosulphite) separates (D. R. P. 278588, 1912).

The hyposulphites can also be prepared in a pure condition by means of a reaction discovered by Moissan (Compt. rend. 1902, 135, 647), which consists in passing a current of sulphur dioxide over metallic hydrides



The hyposulphites of potassium, sodium,

rubidium, caesium, lithium, calcium, and strontium have been obtained in this way.

The free acid is known only in solution; it can be prepared by decomposing a solution of the sodium salt with oxalic acid. A yellow liquid is thus obtained, which soon decomposes, absorbing oxygen from the air with formation of thio-sulphuric acid, which itself rapidly splits up into sulphur and sulphur dioxide.

Constitution and properties of hyposulphites.—Schützenberger in 1869 obtained a crystalline salt to which he assigned the formula NaHSO_2 . Bernsthen, from his own work, regarded the sodium salt as $\text{Na}_2\text{S}_2\text{O}_4$, but as neither chemist had succeeded in preparing the salt in a pure condition, and the percentage composition corresponding to the two formulæ is almost the same, the true formula of the hyposulphites remained uncertain until Nabl succeeded in obtaining a pure zinc salt by passing SO_2 into absolute alcohol in presence of zinc turnings, and established the formula $\text{H}_2\text{S}_2\text{O}_4$ for the acid. This was confirmed by Bernsthen and Balzen (Ber. 1900, 33, 126).

The hyposulphites are to be regarded as derived from a mixed anhydride of sulphurous acid and the hypothetical sulphylic acid $\text{H}\cdot\text{SO}\cdot\text{OH}$, the sodium salt being represented by the formula $\text{O} \begin{smallmatrix} \text{SO}_2\text{Na} \\ \text{SONa} \end{smallmatrix}$. This view of its constitution is borne out by its behaviour towards organic reagents (*see, however, Bucherer and Schwalbe, Ber. 1906, 39, 2814*).

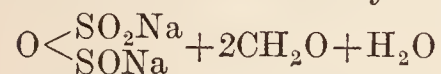
The hyposulphites are strong reducing agents, and on this property their commercial importance depends; both in the solid state when moist, and in aqueous solution, they absorb oxygen rapidly, forming metabisulphites. When added to dilute acid solutions of copper, silver, gold, &c., they precipitate the metal in a colloidal condition; a strong solution of copper sulphate gives a mixture of copper and copper hydride. This latter reaction distinguishes hyposulphurous acid from the other sulphur acids. For the action of sodium hyposulphite on selenium and tellurium, *see* Tschugaev and Chlopin, J. Russ. Phys. Chem. Soc. 1915, 47, 364. For the analysis of solutions containing hyposulphites, *see* Orloff, Chem. Soc. Abstr. 1905, ii. 200; Seyewetz and Block, Bull. Soc. chim. 1906, 35, 293.

For the method of preparing pure sodium hyposulphite from the commercial salt, *see* Jellinek, Zeitsch. anorg. Chem. 1911, 71, 96.

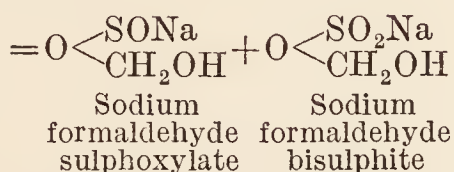
Alkaline pyrogallol may be replaced by a 10 p.c. solution of either zinc hyposulphite or alkaline sodium hyposulphite for the absorption of oxygen in gas analysis. The presence of a little indigotin in the solution of the sodium salt serves to indicate when the reagent should be renewed (Descamps, Bull. Assoc. Chim. Sucr. Dist. 1916, 34, 34).

Sodium hyposulphite. Sodium hyposulphite is now prepared on the large scale for use as a reducing agent in the dyeing and calico-printing industries. It is usually made by the action of zinc on a solution of sodium bisulphite, and subsequent removal of the zinc by milk of lime, the sodium hyposulphite being precipitated from the filtered solution by the addition of salt, when the compound $\text{Na}_2\text{S}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ is obtained. This salt is unstable, but on treating

it with boiling alcohol the water of crystallisation can be removed, and the resulting anhydrous salt is comparatively stable. This latter compound is sold under the name of 'Hydrosulphite BASF,' and contains about 90 p.c. of pure hyposulphite. It is fairly stable in a dry state, but cannot be used in calico-printing as a discharge, as it is oxidised on steaming. This objection was overcome by the discovery of the formaldehyde compounds of sodium hyposulphite, first used at the print-works of Zündel in Moscow. These compounds are obtained by adding a solution of formaldehyde to a solution of sodium hyposulphite. The resulting substance is a mixture in equimolecular proportions of sodium formaldehyde bisulphite and sodium formaldehyde sulphoxylate



Sodium Formaldehyde
hyposulphite



These salts, the mixture of which is sold under the names of Hydrosulphite NF, Rongalite C, &c., are perfectly stable at ordinary temperatures, and are not in themselves reducing agents. On steaming, or boiling with water, they are decomposed into their constituents, and the hyposulphite set free acts as a reducing agent in the usual way. They are employed as discharges for cotton. It was found that by the action of zinc on sodium formaldehyde bisulphite the whole of this could be converted into the sulphoxylate compound which is now manufactured in the above manner, the resulting sodium formaldehyde sulphoxylate being sold as Hydrosulphite NF conc., Hyraldite C extra, &c. It has the formula $\text{NaHSO}_2\text{CH}_2\text{O}, 2\text{H}_2\text{O}$.

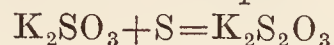
The various commercial brands of hydrosulphite are used as discharges in calico-printing, as stripping agents, and in the dyeing of certain vat colours, such as indigo. Mixtures of the sodium formaldehyde sulphoxylate with small amounts of certain anthraquinone derivatives (which act as catalytic agents), are used for discharging some insoluble azo colours developed on the fibre, *e.g.* α -naphthylamine claret, which resist the action of hydrosulphite alone. Mixtures of the above-named compound with the zinc compounds of some quaternary ammonium bases, such as the zinc compound of dimethylphenylbenzyl-ammonium chloride are used in discharging indigo and other vat dyestuffs, the 'leucotrope,' as it is termed, combining with the reduced dyestuff, and preventing its re-oxidation.

Sodium hyposulphite is also employed as a decoloriser for sugar juice. Malvezin, Rivalland and Grandchamp (Compt. rend. 1921, 173, 1180) recommend zinc-formaldehyde hyposulphite as a reducing agent for dyes such as indigotin as more powerful and more economical in use than hyposulphite. It is prepared by suspending zinc-dust in a 40 p.c. solution of formaldehyde and treating with sulphur dioxide. See also SODIUM, p. 232.

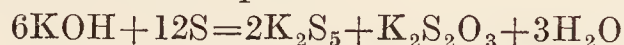
Thiosulphuric acid $\text{H}_2\text{S}_2\text{O}_3$. This acid was first prepared in the form of its sodium salt by

Chaussier in 1799, who obtained it whilst trying to make sodium carbonate by fusing sodium sulphate with carbon. The acid received at first the name of hyposulphurous acid, the present name, thiosulphuric acid, being proposed by Wagner. The free acid is known only in solution, and even this is very unstable and rapidly decomposes with evolution of sulphur dioxide and precipitation of sulphur. Its presence in an acidified solution of a thiosulphate may be shown by adding an aqueous-alcoholic solution of methylene-blue which is decolorised. Sulphurous acid does not effect this reduction. Small quantities of the acid are formed by the action of a solution of sulphurous acid on flowers of sulphur at ordinary temperatures, more rapidly at 80° .

Preparation of thiosulphates.—Thiosulphates may be obtained by boiling solutions of the sulphites with flowers of sulphur



They are also produced, together with polysulphides, by fusing the alkaline carbonates with sulphur, or by boiling the caustic alkalis with water and sulphur



Alkaline and alkaline earth sulphides, particularly the polysulphides, furnish thiosulphates on oxidation either by the oxygen of the air or by suitable oxidising agents.

When iodine acts on a mixture of equimolecular proportions of sodium sulphide and sulphite, a quantitative yield of thiosulphate is obtained (Spring, Ber. 1874, 7, 1157).

Thiosulphates may also be prepared by the electrolysis of ammoniacal sulphite solutions (Halphen, J. Pharm. Chim. 1894, 29, 371).

Properties.—The thiosulphates are mostly soluble in water, and frequently crystallise well. The most important one is the sodium salt commonly known as sodium hyposulphite (*see* under SODIUM, p. 260).

All the soluble thiosulphates contain water of crystallisation, which cannot usually be completely expelled without the salt undergoing decomposition. On strongly heating they all decompose, leaving a mixture of sulphate and sulphide. The same decomposition takes place when their aqueous solutions are boiled for a considerable time, hydrogen sulphide being evolved, and a sulphate remaining in solution. Their solutions are oxidised by mild oxidising agents, such as iodine, and ferric chloride, to tetrathionates (*v. p.* 549), and the electrolytic oxidation of neutral or acid thiosulphate solutions yields the same compounds. Powerful oxidising agents, on the other hand, convert the thiosulphates into sulphates, in some cases with intermediate formation of tetrathionates (Longi, Gazz. chim. ital. 1896, 26, 119). Reducing agents convert them into a mixture of sulphite and sulphide. The constitutional

formula of thiosulphuric acid being $\text{SO}_2 \begin{array}{c} \text{OH} \\ \text{SH} \end{array}$, it might be expected that isomeric thiosulphates, such as $\text{SO}_2 \begin{array}{c} \text{OK} \\ \text{SNa} \end{array}$ and $\text{SO}_2 \begin{array}{c} \text{ONa} \\ \text{SK} \end{array}$ might exist.

According to Schwicker (Ber. 22, 1733), such isomerides have been prepared, but later workers have failed to obtain them, and their existence must at present be regarded as doubtful (*see*

Rohrig, J. pr. Chem. [ii.] 37, 250; Barth, Zeitsch. physikal. Chem. 9, 176; Meyer and Eggeling, Ber. 1907, 1351; Gutmann, *ibid.* 1908, 307).

According to J. C. Gil and J. Beato (Ber. 1923, 56, 2451), if a concentrated solution of sodium thiosulphate (3–4 drops) is added to fuming hydrochloric acid (3–4 c.c.) sodium sulphide is precipitated, after which the clear solution can be preserved without change for about an hour at 15°, and it gives the reactions typical of thiosulphuric acid. An alcoholic solution of thiosulphuric acid is obtained by the action of dry hydrogen sulphide on lead thiosulphate (which has been dried at 105°) suspended in alcohol. The precipitated lead sulphide is filtered off, and excess of hydrogen sulphide is removed from the filtrate by a current of air. The acid decomposes in the course of a few days at about 28° into sulphur and, apparently, pentathionic acid (J. Soc. Chem. Ind. 1924, 43, B. 130).

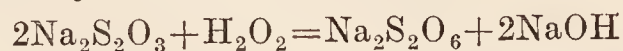
For the ageing of volumetric thiosulphate solutions, see Skrabal (Zeitsch. anal. Chem. 1924, 64, 107; Chem. Soc. Abstr. 1924, 126, ii. 565).

A very large number of double thiosulphates have been prepared and examined, for details as to which the original papers should be consulted (see C. and J. Bhaduri, Zeitsch. anorg. Chem. 1898, 17, 1; Rosenheim and Steinhauser, *ibid.* 1900, 25, 72; Meyer and Eggeling, *l.c.*).

For the determination of thiosulphate in the presence of sulphite, see Kurtenacker (Zeitsch. anal. Chem. 1924, 64, 56; J. Soc. Chem. Ind. 1924, 43, B. 631). See also SODIUM, p. 260.

Dithionic acid $\text{H}_2\text{S}_2\text{O}_6$. This acid was discovered by Welter and Gay-Lussac in 1819. It may be prepared by passing a current of sulphur dioxide through ferric hydroxide suspended in water at a temperature of 0°. At first a reddish-brown solution of ferric sulphite is obtained, which rapidly changes to pale green, the solution then containing ferrous sulphite and dithionate. Baryta water is then added, and the liquid filtered. The calculated quantity of sulphuric acid necessary to precipitate the barium in solution is added to the filtrate, and the resulting solution evaporated *in vacuo* until it attains a sp.gr. of 1.347. On attempting to concentrate it further, it is resolved into sulphur dioxide and sulphuric acid, and its aqueous solution on exposure to air also oxidises with formation of the latter body.

Instead of ferric hydroxide, manganese dioxide can be employed in the above method of preparing dithionic acid, but the yield is then not so satisfactory. The action of sulphur dioxide on various metallic oxides with production of dithionates has been studied by Carpenter (Chem. Soc. Trans. 1902, 1). Dithionates are also obtained by the addition of hydrogen peroxide to a 33 p.c. solution of sodium thiosulphate, the solution being kept neutral during the addition of the peroxide by the simultaneous addition of an acid, the reaction being represented by the following equation



Whilst dithionic acid is not affected by bromine in the cold, it is completely oxidised to sulphuric acid by bromates in boiling hydrochloric acid solution. A measured quantity of

bromate is employed, the excess of liberated bromine being distilled over into iodide solution and determined in the usual manner. The method allows of a high order of accuracy. If sulphurous and thiosulphuric acids be present, in addition to the oxidation at the boiling-point by bromine, a second oxidation with bromine in the cold is carried out (this oxidises the latter two acids only, forming sulphuric acid in each case), and an iodine oxidation in the cold, which oxidises sulphurous to sulphuric acid, and thiosulphuric to tetrathionic acid. From the quantities of halogen required in each of the three cases, the quantities of dithionic, sulphurous, and thiosulphuric acids present may be calculated (C. Mayr and Szentpaly-Peyfuss, Zeitsch. anorg. Chem. 1924, 131, 203; Chem. Soc. Abstr. 1924, 126, ii. 201).

The dithionates are most easily obtained from the barium salt, by double decomposition with the sulphate of the corresponding base. Only the neutral salts are known. They are all soluble in water, and usually crystallise well, all except the potassium salt containing water of crystallisation. Their solutions are not oxidised by atmospheric oxygen in the cold, but on heating a sulphate is produced; nascent hydrogen reduces dithionates to sulphites. On heating the dry salts they decompose, partially at 100°, completely at a higher temperature, evolving sulphur dioxide and leaving a residue of sulphate.

The formation of dithionate by heating silver sulphite or silver-sodium sulphite shows that dithionic acid is composed of two sulphonyl radicles $(\text{SO}_3\text{H})_2$, and has not the formula SO_2OH assigned to it by Kolbe (Baubigny, Compt. rend. 1910, 150, 973).

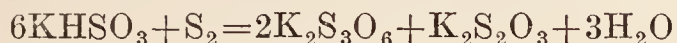
Dithionic acid may be separated from the other thionic acids by treatment of the mixture with alkaline permanganate, or sodium hypobromite. A solution of barium acetate is then added, and the barium sulphate filtered off. The filtrate contains the dithionate.

The estimation of dithionates may be made volumetrically as follows: The sample is weighed into a flask, covered with hydrochloric acid (1:1) free from chlorine, and a current of carbon dioxide passed through the apparatus. The flask is heated, the flow of carbon dioxide being checked when the evolution of sulphur dioxide begins. The latter is absorbed in excess of standard iodine solution. Finally the apparatus is swept over with carbon dioxide. The reaction $\text{Na}_2\text{S}_2\text{O}_6 = \text{Na}_2\text{SO}_4 + \text{SO}_2$ only begins on heating (Fischer and Classen, Zeitsch. angew. Chem. 1922, 35, 198; J. Soc. Chem. Ind. 41, 1922, 413 A).

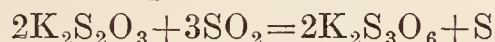
Literature.—Welter and Gay-Lussac, Ann. Chim. 1819, 10, 312; Gélis, *ibid.* 65, 222; Spring and Bourgeois, Bull. Acad. Roy. 1878, 45, 151; Meyer, Ber. 34, 3606; Hauer, J. pr. Chem. [i.] 80, 229; Péan de Saint-Gilles, Ann. Chim. [ii.] 55, 374; Buignet, J. Pharm. Chim. 38, 122; Fordos and Gélis, *ibid.* 36, 113; Dymond and Hughes, Chem. Soc. Trans. 71, 314; Jacquelin, Ann. Chim. [iii.] 21, 110; Rathke and Zschiesche, J. pr. Chem. 92, 141; Otto, Annalen, 147, 187; Kolbe, J. pr. Chem. [i.] 19, 484; Heeren, Pogg. Ann. 7, 191; Carpenter, Chem. Soc. Trans. 1902, 1; Friessner, Zeitsch. Elektrochem. 10, 265.

Thionic acids. The constitution of thionic acids is discussed by Vogel (Chem. News, 1924, 128, 325; Chem. Soc. Abstr. 1924, ii. 470).

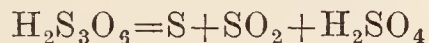
Trithionic acid $\text{H}_2\text{S}_3\text{O}_6$. This compound was discovered by Langlois in 1842, who obtained the potassium salt by gently heating a solution of potassium bisulphite with sulphur



The reaction probably takes place in two stages, in the first of which the thiosulphate is formed, and this is then converted into trithionate by the action of sulphur dioxide. This view is supported by the fact that potassium trithionate can be obtained by acting on the thiosulphate with sulphur dioxide:



The sulphur then acts further on the trithionate to form tetra- and pentathionate (Plessy). The free acid may be prepared by adding hydrofluosilicic acid to a solution of the potassium salt, when insoluble potassium silicofluoride is precipitated, and trithionic acid set free. The dilute solution of the acid thus obtained is stable, but on attempting to concentrate it, even *in vacuô*, it decomposes into sulphur, sulphur dioxide, and sulphuric acid



It has no smell, but possesses a strongly bitter taste.

Preparation of trithionates.—A convenient way of preparing trithionates consists in acting on a thiosulphate with a persulphate, the former salt being kept in excess, when a good yield of trithionate is obtained (Marshall, J. Soc. Chem. Ind. 1897, 16, 396).

Certain double thiosulphates undergo decomposition when boiled with water, producing trithionates. Colefax has shown (Chem. Soc. Trans. 1892, 181, 1083; 1908, 811) that iodine does not oxidise a mixture of sodium sulphite and thiosulphate directly to trithionate, as was formerly thought to be the case, but that when the iodine is present in insufficient quantity to convert all the sulphite into sulphate, the residual sulphite abstracts sulphur from the tetrathionate (formed by oxidation of the thiosulphate) to produce a trithionate. According to Willstätter (Ber. 1903, 36, 1831) the oxidation of sodium thiosulphate by hydrogen peroxide gives rise to trithionate and sulphate.

Properties.—The trithionates are all soluble in water, with the exception of the silver and mercury salts, and frequently crystallise well. Their solutions oxidise on exposure to air, forming sulphates and liberating sulphur and sulphur dioxide, and the same decomposition ensues on heating the solid salts. Sodium amalgam converts the salts into a mixture of sulphite and thiosulphate, whilst sodium arsenite or stannite reduces them completely to sulphites (Gutmann, Ber. 1905, 38, 1728, 3277).

The trithionates of potassium, rubidium, and caesium have been prepared and crystallographically examined by Mackenzie and Marshall (Chem. Soc. Trans. 1908, 1726). See also Plessy, J. pr. Chem. 1844, [i.] 33, 348; Chancel and Diacon, Compt. rend. 1863, 56, 710; Fordos and Gélis, *ibid.* 1843, 16, 1070; Rathke, J. pr. Chem. 1865, [i.] 95, 1; Hertlein, Zeitsch. physikal. Chem. 1896, 19, 287.

Tetrathionic acid $\text{H}_2\text{S}_4\text{O}_6$. This acid was discovered in 1843 by Fordos and Gélis, who also prepared certain of its salts. They obtained it from its barium salt, which is formed when iodine acts on barium thiosulphate suspended in water: $2\text{BaS}_2\text{O}_3 + \text{I}_2 = \text{BaS}_4\text{O}_6 + \text{BaI}_2$. The thiosulphate of lead is, however, preferable to that of barium in preparing the acid, since the latter salt gives rise to the simultaneous formation of a little trithionate as well. The lead thiosulphate is suspended in water and iodine carefully added, when soluble lead tetrathionate and insoluble lead iodide are produced. The liquid is filtered, the lead in the filtrate precipitated by the addition of a slight excess of sulphuric acid, and the excess of the latter removed by the cautious addition of baryta water. The solution of the free acid thus obtained may be concentrated by evaporation *in vacuô*. Tetrathionic acid is only known in the form of its aqueous solution; this is colourless, odourless, and strongly acid. On concentration beyond a certain point it decomposes in a similar manner to trithionic acid. Sulphuric acid and hydrochloric acid have no action on it in the cold; on heating, this latter acid disengages hydrogen sulphide. Oxidising agents, such as nitric acid, convert tetrathionic acid into sulphuric acid, while reducing agents (sodium amalgam) form thiosulphate.

Preparation.—The tetrathionates are formed by the partial oxidation of thiosulphates, a convenient oxidising agent being potassium persulphate (Marshall, J. Soc. Chem. Ind. 1897, 16, 396) $\text{K}_2\text{S}_2\text{O}_8 + 2\text{BaS}_2\text{O}_3 = 2\text{BaSO}_4 + \text{K}_2\text{S}_4\text{O}_6$. If an excess of thiosulphate be employed a trithionate is produced (*v. supra*).

According to Sander (Zeitsch. angew. Chem. 1915, 28, 273) pure sodium and potassium tetrathionates can be made by adding drop by drop to a cooled solution of 26 grms. of iodine in alcohol, a saturated solution in water of 50 grms. of sodium thiosulphate or 39.5 grms. of potassium thiosulphate. The tetrathionate, which separates out as it is formed, is collected and washed with alcohol until it is free from iodine and iodide, dissolved in a little water and again precipitated by alcohol.

The electrolytic oxidation of thiosulphates in neutral or acid solution also gives rise to tetrathionates, the oxidation under these conditions not proceeding further (Thatcher, Zeitsch. physikal. Chem. 1904, 47, 641).

The interaction of sulphite and tetrathionate yields thiosulphate and trithionate. A solution of the tetrathionate is mixed with a solution of sodium sulphite and alcohol. After 5 minutes, formaldehyde and acetic acid are added to combine with the excess of sulphite and the liquid is titrated immediately with 0.1 N-iodine solution.

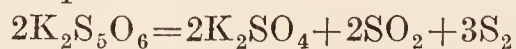
Pentathionates may be determined in a similar manner (A. Kurtenacker, Zeitsch. anorg. Chem. 1924, 134, 265–268; Chem. Soc. Abstr. 1924, ii. 497–498).

Properties.—The tetrathionates are all soluble in water; their solutions oxidise on exposure to air, forming sulphate, thiosulphate, and other products. On boiling the solution, the products are sulphur dioxide, sulphur, and a sulphate (Gutmann, Ber. 1908, 41, 300).

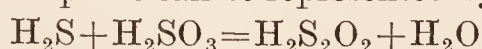
The dry salts decompose on heating into

mixtures of dithionates and trithionates, or, in the case of the tetrathionates of the heavy metals, into sulphide and sulphate. A number of inorganic and organic tetrathionates have been described by Calzolari (Atti R. Accad. Lincei, 1915, [v.] 24, i. 921). For the action of hydroxylamine with sodium tetrathionate, see Gutmann (Ber. 1920, 53, B. 444; Chem. Soc. Abstr. 1920, ii. 307).

Pentathionic acid $\text{H}_2\text{S}_5\text{O}_6$. This acid was discovered by Wackenroder in 1846. It is obtained by passing a slow current of hydrogen sulphide into water which has been previously almost saturated with sulphur dioxide, allowing the liquid to stand for some time, then again passing in sulphur dioxide, and repeating this cycle of operations several times. The liquid so obtained contains in addition to pentathionic acid, free sulphur, both in solution and in suspension, sulphuric acid, thiosulphuric acid, and small amounts of tri- and tetrathionic acids, possibly also hexathionic acid. The liquid is filtered as far as possible from the sulphur, and a little freshly-precipitated barium carbonate added, which precipitates the sulphuric acid formed, together with the remainder of the sulphur, which is removed along with the barium sulphate by filtration. The clear filtrate is concentrated on a water-bath until it attains a sp.gr. of 1.32, and the concentration is then continued *in vacuô* at the ordinary temperature to a sp.gr. of 1.46, when the residual liquid consists mainly of pentathionic acid (Wackenroder, Ann. Chim. 1846, 60, 189; Kessler, Pogg. Ann. 74, 249; Takamatsu and Smith, Chem. News, 1880, 41, 290; Lewes, Chem. Soc. Trans. 39, 68; 41, 300). On attempting to concentrate it further, or on heating its solution, the acid decomposes into sulphuric acid, sulphur dioxide, hydrogen sulphide, and sulphur. On adding, with constant stirring, to the concentrated solution of the acid about half the quantity of caustic potash required for complete neutralisation, and filtering from any precipitated sulphur, the clear liquid gives on spontaneous evaporation well-defined crystals of potassium pentathionate $\text{K}_2\text{S}_5\text{O}_6 \cdot \text{H}_2\text{O}$ (Lewes). This salt can be recrystallised from solutions at 50° containing a little free sulphuric acid, but it is at once decomposed in the presence of alkalis. A better method of obtaining the salt consists in adding potassium acetate instead of caustic potash to the concentrated solution of the acid. The potassium salt dissolves in about twice its weight of water to form a clear neutral solution, which decomposes on standing, more quickly on heating, forming a tetrathionate and free sulphur. The dry salt, if freed from water by washing with alcohol, is much more stable, and can be kept unaltered for a long time. On heating the salt it evolves sulphur dioxide and sulphur, and leaves a sulphate:

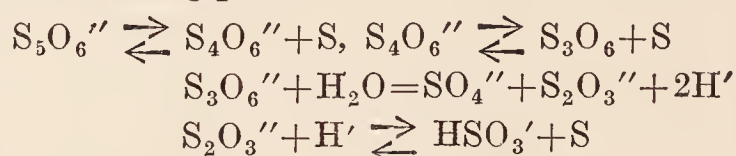


The reaction between sulphurous acid and hydrogen sulphide can be represented by

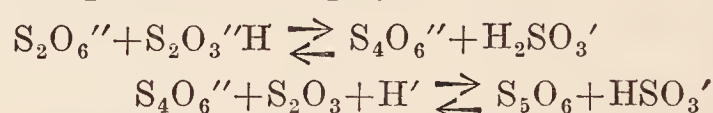


Further reaction with hydrogen sulphide produces sulphur, whereas excess of sulphurous acid leads to the formation of pentathionic acid. Of the polythionic acids and their alkali salts,

the tetrathionates are the most stable, and the trithionates the most unstable; the pentathionates occupying an intermediate position. None of these compounds is completely stable in aqueous solution, the following decompositions taking place:

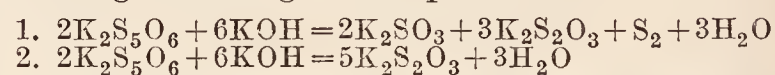


The insolubility of sulphur removes it from the equilibrium, and at boiling temperature the sulphur dioxide is removed and SO_4'' is alone left in solution; side reactions also take place. The more sulphur dioxide and sulphur remains in the solution, the greater is the tendency of thiosulphuric acid to polymerise, *e.g.*



A high concentration of hydrogen-ion retards the decomposition of tetra- and pentathionic acids, but not of trithionic acid (Foerster and Hornig, Zeitsch. anorg. Chem. 1922, 125, 86; Chem. Soc. Abstr. 1923, 123, ii. 23).

Oxidising agents convert pentathionates into sulphates. Caustic soda decomposes pentathionates, the action varying with the conditions. With dilute alkali a tetrathionate and sulphur are produced in the cold; sulphur and a trithionate on heating. With an excess of alkali a thiosulphate and sulphite are formed, or on heating to boiling, thiosulphate alone.



Sodium amalgam converts pentathionates into thiosulphates; or on continued action, into sulphides.

Pentathionic acid is also produced by the action of hydriodic acid and iodine, or hydrogen sulphide, on lead thiosulphate (Persoz; Takamatsu and Smith).

The toxicity of sulphur when used as a fungicide for the control of disease upon plants, appears to be due to pentathionic acid formed by the oxidation of the sulphur (H. C. Young, Nature, 1923, 634).

The pentathionates have been little examined; the copper salt $\text{CuS}_5\text{O}_6 \cdot 4\text{H}_2\text{O}$ forms small blue crystals, easily soluble in water (Debus).

Hexathionic acid $\text{H}_2\text{S}_6\text{O}_6$. The possible existence of the potassium salt of this acid in the mother-liquor of Wackenroder's solution has been indicated by Debus (Chem. Soc. Trans. 1888, 53, 278), but neither the acid nor any of its salts have been prepared in a pure condition. The potassium salt is said to form a warty, non-crystalline mass, which readily decomposes in solution, even in the presence of dilute sulphuric acid.

According to Riesenfeld and Feld, hexathionic acid does not exist, the so-called hexathionate solutions being probably pentathionate containing sulphur in colloidal solution.

Takamatsu and Smith (*ibid.* 37, 608) give a table (p. 519) of reactions to distinguish tetra- and pentathionic acids from each other, and from the other thionic acids.

For the estimation of polythionates in presence of thiosulphate and free sulphur dioxide,

see Feld, Zeitsch. angew. Chem. 1913, 26, 286; cf. Sander, *ibid.* 1915, 29, 8; Chapin, J. Amer. Chem. Soc. 1916, 38, 625; Billeter and Wavre, Helv. Chem. Acta, 1918, 1, 174; Riesenfeld and Feld, Zeitsch. anorg. Chem. 1921, 119, 225.

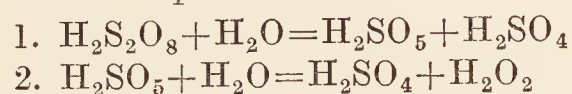
Literature.—Plessy, Compt. rend. 21, 473; Ann. Chim. [iii.] 20, 162; Thomson, Ann. Phil. 12, 441; Lenoir, Annalen, 62, 253; Ludwig, Arch. Pharm. 51, 259; Fordos and Gélis, Ann. Chim. [iii.] 22, 66; 28, 451; Rister-Bennet, Pogg. Ann. [ii.] 116, 470; Chancel and Diacon, Compt. rend. 56, 710; Rammelsberg, J. 10, 136; W. Spring, Ber. 6, 1, 108; Annalen, 199, 97; 213, 329; Stingl and Morawski, J. 1879, 1110; Curtius, J. pr. Chem. [ii.] 27, 25, 225; Shaw, Chem. Soc. Trans. 43, 351; Smith, *ibid.* 43, 355; Salzer, Ber. 1886, 1696; Kessler, Pogg. Ann. [ii.] 74, 294; Takamatsu and Smith, Chem. Soc. Trans. 1880, 37, 592; Lewes, *ibid.* 1882, 300; Shaw, *ibid.* 1883, 351; Valetton, Chem. Soc. Abstr. 1907, ii. 811.

Sulphur heptoxide S_2O_7 . This oxide of sulphur was discovered by Berthelot, who obtained it by submitting a mixture of equal volumes of SO_2 and O to the silent electric discharge. It forms a viscid liquid, which becomes solid at 0° , forming white, crystalline needles. It is very volatile, and decomposes slowly at the ordinary temperature, rapidly on heating, into sulphur trioxide and oxygen, but may be kept unchanged for some time at a low temperature. Water decomposes it with formation of sulphuric acid and oxygen.

According to Meyer, Bailleul and Henkel (Ber. 1922, 55, 2923), when sufficient energy is

imparted the action of the silent electrical discharge on a mixture of sulphur dioxide and oxygen leads to the formation of more highly oxidised substances than sulphur heptoxide. Berthelot's heptoxide was possibly a mixture of sulphur trioxide and sulphur tetroxide in equimolecular proportions.

Persulphuric acid. A solution of this acid is obtained by the electrolysis of dilute sulphuric acid, and its formation was observed by Berthelot, although he did not isolate it. It is best prepared by the electrolysis of an acid of sp.gr. 1.35–1.50, the current density being 100 ampères per square decimetre (Elbs and Schönherr, Zeitsch. Elektrotech. and Elektrochem. 1895, 245, 468). The electrolysis should be rapid and the solution should be cooled. The anode should be of smooth platinum. It gradually loses its efficiency, which, however, may be recovered on ignition. An essential condition of success is that the potential difference between the anode and the solution should be high (cf. Müller and Emslander, Zeitsch. Elektrochem. 1912, 18, 752). It slowly undergoes decomposition in solution into sulphuric acid and Caro's acid, which itself slowly breaks up into hydrogen peroxide and sulphuric acid



By the electrolysis of sulphuric acid (d 1.44) between a platinum anode and an aluminium cathode with a current of 3.5–4.0 amps. at 8–12 volts, a solution of persulphuric acid is obtained which decomposes on warming first

Reagents	Dithionic acid $H_2S_2O_6$	Trithionic acid $H_2S_3O_6$	Tetrathionic acid $H_2S_4O_6$	Pentathionic acid $H_2H_5O_6$
Cautic potash .	No. ppt.	No ppt.	No ppt.	Immediate ppt. of sulphur No action
Dilute hydrochloric acid	No action	Evolution of SO_2 , and ppt. of S	No action	
Mercurous nitrate	No ppt.	Immediate black ppt., turning white on standing	Yellow ppt., gradually darkening	Yellow ppt. at first, turning white with excess of reagent on standing
Silver nitrate .	No ppt.	Yellow ppt., soon turning black	Yellow ppt., soon turning black; also blackened on adding ammonia	Yellow ppt., gradually darkening; black on adding ammonia
Ammoniacal silver nitrate	—	No brown colour, even on standing. On warming, Ag_2S formed	No brown colour, even on standing, unless warmed	Almost immediate brown coloration, turning black on warming
Mercuric cyanide	No ppt.	—	At first, yellow ppt.; turns black on warming, with evolution of HCN	At first, yellow ppt.; gradually turns black on warming with evolution of HCN
Mercuric chloride	No ppt.	Yellow ppt., turning white with excess of reagent	White ppt. on warming	Whitish-yellow ppt. on warming
Potassium hydrosulphide	—	—	White ppt. of sulphur	White ppt. of sulphur
Dilute potassium permanganate solution	One drop, immediate brown ppt.	One drop, immediate brown ppt., even in presence of dilute H_2SO_4	Decolorised, without addition of dilute H_2SO_4 . No ppt.	Decolorised, without addition of dilute H_2SO_4 . No ppt.

to permonosulphuric acid (Caro's acid), then to sulphuric acid with the formation of hydrogen peroxide. Distillation of this solution (containing 2.0–3.5 grms. of active oxygen per litre) at 65°–90°/50–100 mm. yields a distillate that contains about 0.5 p.c. of hydrogen peroxide and an acid solution that may be used again. Redistillation gives a liquid containing 24 p.c. of hydrogen peroxide. The current yield using technical sulphuric acid without cooling was 65 p.c., which fell to 40 p.c. after the first, and to 23 p.c. after the second distillation (A. Brodsky, *Zeitsch. angew. Chem.* 1924, 37, 270; *Chem. Soc. Abstr.* 1924, 126, ii. 403).

For the rate of decomposition, *see* Palme, *Zeitsch. anorg. Chem.* 1920, 112, 97.

A solution of the acid can also be obtained by decomposing barium persulphate with the theoretical quantity of dilute sulphuric acid.

Persulphuric acid is obtained in an almost pure condition by the action of 100 p.c. hydrogen peroxide on well-cooled chlorosulphonic acid (*see* under *Caro's acid*). It forms a white, crystalline mass, melting with decomposition at a little above 60°. At the ordinary temperature it is stable and can be kept for months.

Persulphuric acid is formed during the working of accumulators (Robertson, *Proc. Roy. Soc.* 1892, 105). For the determination of persulphuric acids, *see* R. Wolffenstein and V. Makow, *Ber.* 1923, 56, 1768–1771.

Persulphates. The persulphates were first prepared in 1898 by Hugh Marshall, who discovered that crystals of the potassium salt were formed at the anode during the electrolysis of a solution of the sulphates of potassium and cobalt in a 'divided cell'; and also by the electrolysis of a saturated solution of potassium bisulphate in the same apparatus. The ammonium salt was prepared by replacing the KHSO_4 by ammonium sulphate and dilute sulphuric acid. By treating a saturated solution of the ammonium salt with barium hydroxide Marshall obtained the barium salt, the excess of baryta being removed by a current of carbon dioxide. The lead salt was obtained by decomposing a solution of the barium salt with sulphuric acid and neutralising the liquid with lead carbonate. By acting on the barium salt with zinc sulphate a solution of the zinc salt was obtained.

The persulphates are now manufactured on the large scale for use as oxidising agents. The potassium salt is prepared, as stated above, by electrolysis of a solution of potassium bisulphate in a divided cell. If the anode potential be raised by the addition of hydrofluoric acid to the liquid, the yield of persulphate is greatly increased, and the diaphragm can be dispensed with. A current density of 5 ampères per square cm. gives a good yield of persulphate. Ammonium persulphate is prepared in a similar manner by electrolysis of a solution of ammonium sulphate in dilute sulphuric acid (1 : 7) in a divided cell, the inner compartment containing the anode and the ammonium salt, the outer cell the cathode, and dilute acid alone. In the preparation of persulphates by electrolysis, the yield gradually falls off, owing to the formation of Caro's acid; the essential conditions for obtaining a satisfactory yield are, that the current

density at the anode should be high, the anode itself small, and that the solution should be kept cool (*see* Elbs and Schonherr, *l.c.*; Blumer, *Zeitsch. Elektrochem.* 1911, 17, 965; Schall and Andrich, *Chem. Zeit.* 1912, 36, 645).

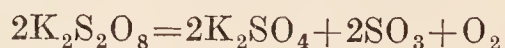
J. Salanze (*Bull. Soc. chim.* 1923, 33, [iv.] 1738) has made an extensive investigation of the electrolytic preparation of ammonium persulphate by different methods. The preparation may be effected either in acid or in neutral solution (chromate method, Müller, A. 1912, ii. 895, etc.). The second method gives the higher yield (80–85 p.c.), but has many disadvantages. The chromium hydroxide diaphragm formed on the cathode (which must be off platinum) is very fragile, and dissolves if the solution becomes slightly acid. Temperature has little effect on the yield, which is as good at 22° as at 8°, whilst the yield is improved if chlorides are added in traces. The process can only be followed by measuring (1) the gas evolved, or (2) the cathode potential, which necessitates continued attention. Another drawback to the method is due to the great solubility of ammonium persulphate in neutral or alkaline solution. Prolonged electrolysis is needed before the salt separates.

Electrolysis in acid solution does not require much attention, and the ammonium persulphate separates readily. Electrolysis may be effected in presence or in absence of potassium ferrocyanide, addition of the latter increasing the yield, but giving a product slightly contaminated with Prussian-blue, which is difficult to remove. The conditions for a good yield (70–75 p.c.) are as follows: (1) a low temperature, (2) a concentration of sulphuric acid corresponding with the presence of ammonium hydrogen sulphate, (3) a fresh platinum anode (anodic current density, 50 amps. per sq. dm.), (4) a platinum cathode and (this being very important) the largest possible cathodic current density, and (5) the presence of a trace of chloride-ion (*Chem. Soc. Abstr.* 1924, 126, ii. 177).

According to D. R. P. 271642 (*Farbf. vorm. Fried. Bayer & Co.*) the electrolytic preparation of persulphates can be carried out without the addition of electrolytes or the use of a diaphragm if tin or aluminium cathodes are employed.

Lithium persulphate cannot be obtained in this manner, since although the salt is formed it cannot be isolated from the solution (Otin, *Zeitsch. Elektrochem.* 1911, 919).

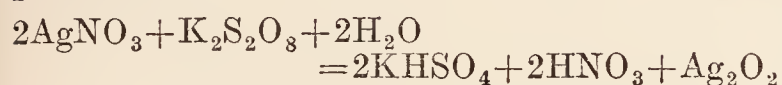
The persulphates are all soluble in water, the least soluble being the potassium salt, which requires about 56 parts of water at 0° for solution. Their solutions slowly decompose on standing with evolution of oxygen and formation of a sulphate and free sulphuric acid, and the same change takes place rapidly on boiling the liquid. The dry salts decompose on heating according to the following equation



The alkaline persulphates can, however, be preserved unchanged if kept dry and protected from light. The molecular formula of the persulphates has been found from electrical conductivity measurements to be $\text{R}_2\text{S}_2\text{O}_8$ and not RSO_4 (Löwenherz, *Chem. Zeit.* 16, 838).

Solutions of the persulphates give no precipitate with barium chloride; on warming,

however, barium sulphate slowly separates out, and oxygen is evolved. An alkaline lead solution gives a precipitate of the peroxide on boiling. Barreswil's (Fehling's) solution gives a red precipitate of cuprous oxide. Ferrous sulphate is rapidly oxidised to ferric sulphate, with rise of temperature. Persulphates and iodates react to form sulphates and periodates. (For the estimation of periodates in presence of persulphates, *see* Müller and Jacob, *Zeitsch. anorg. Chem.* 1913, 82, 308.) In the absence of iodides and perchlorates, persulphates yield a red precipitate with methylene-blue solution. To identify a persulphate in presence of a perchlorate, an alcoholic benzidine solution is poured on the surface of the solution; a blue precipitate appears at the junction of the two liquids if a persulphate is present. Solutions of manganous, nickel and cobalt salts all yield precipitates of the higher oxides when mixed with a persulphate and warmed, and chromium compounds are oxidised to chromates. Persulphuric acid oxidises many organic bodies, converting alcohol into aldehyde, and aniline into a brown colouring matter, and bleaching indigo, litmus, and turmeric solutions. Paper and cloth become quite rotten after being dipped in a solution of a persulphate. Silver nitrate gives, with potassium persulphate, a black precipitate of silver peroxide



If, however, a strong solution of ammonium persulphate is treated with ammonia and a small amount of silver nitrate, a vigorous evolution of nitrogen takes place, and the liquid becomes heated to boiling. Silver peroxide is first formed, and this oxidises the ammonia to water, setting free nitrogen. For the action of solutions of persulphates on metallic silver, *see* Higson, *Chem. Soc. Trans.* 1921, 119, 2048.

By warming a persulphate with concentrated sulphuric acid the oxygen is liberated largely in the form of ozone. With hydrochloric acid chlorine is evolved.

Persulphuric acid may be distinguished from hydrogen peroxide on the one hand, and Caro's acid on the other, by its neither giving a reddish-brown coloration with a solution of a titanium salt, nor reducing a dilute solution of potassium permanganate, whilst it does not immediately liberate iodine from an acidified solution of potassium iodide.

Commercial ammonium persulphate may be purified by making a saturated solution of the salt at 90°, adding ammonia to neutralise the free acid present (due to the partial decomposition of the persulphate), filtering, allowing to cool to 30°, and then adding twice the bulk of alcohol and cooling with ice applied externally. The crystals which separate out are well drained and washed with alcohol and ether, and allowed to dry in the air.

The potassium salt has been employed in photography to remove the last traces of the sodium thiosulphate from negatives after fixing. For the iodometric estimation of persulphuric acid, *see* Müller and v. Ferber, *Zeitsch. anal. Chem.* 1913, 52, 195; Müller, *ibid.* 1913, 58, 299.

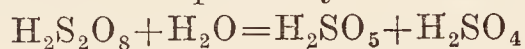
Literature.—Berthelot, *Compt. rend.* 86, 20,

71, and 277; 112, 1418; Traube, *Ber.* 22, 1518; 24, 1764; Mendeléeff, *Bull. Soc. chim.* [iii.] 38, 168; Marshall, *Chem. Soc. Trans.* 1891, 771; Richarz, *Ber.* 21, 1670; Bredig, *Zeitsch. physikal. Chem.* 1893, 12, 230; Moeller, *ibid.* 1893, 12, 255; Schoop, *Zeitsch. Elektrochem.* 1895, 273; Lowry and West, *Chem. Soc. Trans.* 1900, 77, 950; Armstrong and Lowry, *Chem. News*, 1902, 85, 193; Price, *Per-acids and their Salts* (Longmans); Prideaux, *J. Soc. Chem. Ind.* 1918, 257 R.

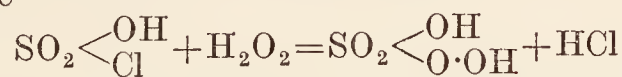
Monopersulphuric acid or Caro's acid H_2SO_5 . This acid was discovered by Caro in 1898, whilst studying the action of sulphuric acid on persulphates, and was more fully investigated by Baeyer and Villiger (*Ber.* 1901, 34, 853).

A solution of the acid can be obtained by triturating 10 grms. of potassium persulphate with 20 grms. of concentrated sulphuric acid, allowing the mixture to stand for an hour, pouring it upon ice, and removing the sulphuric acid from the resulting solution by the addition of barium phosphate. The solution thus prepared, containing free phosphoric acid, is tolerably stable, and only very slowly undergoes hydrolysis into hydrogen peroxide and sulphuric acid.

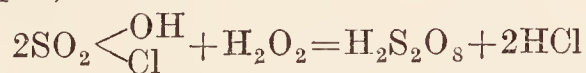
Monopersulphuric acid is also formed during the electrolysis of moderately concentrated sulphuric acid; if an acid of sp.gr. 1.4 be electrolysed, persulphuric acid is first produced, and this is then decomposed by the water present



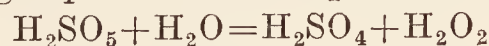
The acid has been prepared in a nearly pure state by D'Ans and Friedrich (*Ber.* 1910, 43, 1880) by the subjoined method. The calculated amount of 100 p.c. hydrogen peroxide is added to well-cooled chlorosulphonic acid, when an evolution of hydrogen chloride takes place. The mixture is allowed to become warm, and the dissolved hydrochloric acid sucked off at the pump. The residue then solidifies to a colourless, crystalline mass, melting at about 45° with slight decomposition. The acid thus prepared has a purity of about 98 p.c. The following equation represents the reaction taking place—



By using twice the quantity of chlorosulphonic acid persulphuric acid is produced (*v. supra*)—



Properties.—Monopersulphuric acid is slowly decomposed in aqueous solution with production of hydrogen peroxide and sulphuric acid



This reaction is, however, a balanced one, as a mixture of hydrogen peroxide and concentrated sulphuric acid forms some Caro's acid. It may be distinguished from hydrogen peroxide by its not giving the reddish-brown coloration with titanium salts, and from persulphuric acid by its causing an *immediate* liberation of iodine from an acidified solution of potassium iodide; further, monopersulphuric acid converts aniline into nitrosobenzene, whereas persulphuric acid under similar conditions only produces a brown

colouring matter. This reaction takes place more easily with *p*-substituted anilines, such as *p*-bromaniline, than with aniline itself (Morgan).

A mixture of monopersulphuric acid and potassium permanganate forms one of the most powerful oxidising solutions known.

No salts corresponding to this acid have as yet been obtained.

The formula assigned to Caro's acid by Baeyer and Villiger was H_2SO_5 . Other chemists (Armstrong and Lowry, *Chem. News*, 1902, 85, 193; Lowry and West, *Chem. Soc. Trans.* 1900, 950) regarded it as $\text{H}_2\text{S}_2\text{O}_9$ or $\text{H}_2\text{S}_4\text{O}_{14}$ ($\text{H}_2\text{O}_2, 4\text{SO}_3$). The formula H_2SO_5 has, however, been established by Slater Price (*Ber.* 1902, 291) and D'Ans and Friedrich (*ibid.* 1910, 880).

According to Armstrong and Robertson (*Proc. Roy. Soc.* 1892, 50, 105) a series of persulphuric acids exist. The acid $\text{H}_2\text{O}_2, 4\text{SO}_3$ is supposed to be formed in the presence of strong sulphuric acid and by dilution, acids of the type $\text{H}_2\text{O}_2, 3\text{SO}_3$, $\text{H}_2\text{O}_2, 2\text{SO}_3$, &c., are successively obtained.

If a persulphate in the state of powder be treated with 100 p.c. sulphuric acid in the cold, a mass possessing a strong odour, recalling that of chloride of lime, is produced. This substance has quite different properties from Caro's acid; thus it reduces potassium permanganate and gives a reddish-brown coloration with titanium salts. The composition of this body has not been definitely established, but according to Baeyer and Villiger its behaviour is possibly due to the presence of a higher oxide of sulphur of the formula S_2O_8 .

A method to determine hydrogen peroxide, persulphuric acid, and monopersulphuric acid, when all three are present in solution, has been devised by Baeyer and Villiger (*l.c.*). The amount of monopersulphuric acid present is first determined by adding an acidified solution of potassium iodide, and immediately titrating the liberated iodine with sodium thiosulphate and starch paste. The solution thus decolorised slowly turns blue again on standing, and after 12–24 hours it is again titrated, the iodine now representing the amount of persulphuric acid present. In another portion the hydrogen peroxide is estimated by titration with potassium permanganate. Though not strictly accurate, the method yields satisfactory results. See also R. Wolfenstein and V. Makow (*Ber.* 1923, 56, [B], 1768–1771; *J. Chem. Soc.* 1923, 123, 124; Abstracts, ii. 652).

SULPHURIC ACID. Sulphur trioxide, or sulphuric anhydride, the substance indicated by the formula SO_3 , and consisting of 40 parts of sulphur and 60 parts oxygen, combines with water energetically to form a series of products capable of representation by the formula $m\text{SO}_3, n\text{H}_2\text{O}$. Some of these hydrates in which *m* and *n* have certain simple integral values are usually recognised as distinct compounds, either on account of certain well-marked physical properties or because of the existence of definite metallic salts derived from them by replacement of the hydrogen by metals, whilst others are considered to be mixtures of these hydrates, or solutions of one or other of them in excess of water.

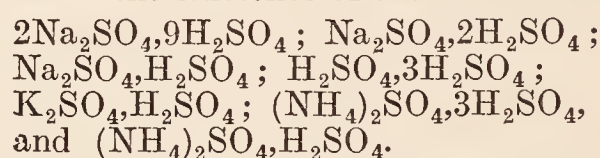
There is strong evidence that at great

dilution sulphuric acid dissociates into two H^+ and one SO_4^{--} ions. This is substantiated by the close agreement of the measured and calculated potentials (Ferguson and France, *J. Amer. Chem. Soc.* 1921, 43, 2150).

Starting from sulphur trioxide SO_3 , which is a crystalline solid, melting at 14.8° , when quite pure and free from water, the more generally accepted compounds are—

Pyrosulphuric acid $2\text{SO}_3, \text{H}_2\text{O}$. A crystalline solid melting at 35° , the melting-point being lowered on the addition of SO_3 or H_2O . Pyrosulphuric acid forms definite crystalline salts, known as the pyrosulphates.

Pyrosulphates cannot be prepared in the pure state by dehydration of the acid sulphates, even under reduced pressure or in a current of sulphur trioxide. Sodium pyrosulphite, obtained synthetically from the anhydrous sulphate and sulphur trioxide, melts at 400.9° and has d_4^{25} 2.658, and potassium pyrosulphate melts at 414.2° and has d_4^{25} 2.512. The reciprocal solubilities of sodium bisulphate and pyrosulphate and those of the corresponding potassium salts are given, together with the results of an investigation into the phenomena of the fusion and solidification of binary mixtures of sulphuric acid with sulphates of sodium, potassium, and ammonium; confirmation is obtained of the existence of the double salts,



The pyrosulphates form no compounds with the bisulphates (L. Cambi and G. Bozza (*Annali Chim. Appl.* 1923, 13, 221–238); *J. Soc. Chem. Ind.* 1924, 43, B, 14).

Sulphuric acid $\text{SO}_3, \text{H}_2\text{O}$. A liquid at the ordinary temperature, but solidifying at about 10.5° , and also forming a large number of well-defined salts, the neutral and acid sulphates.

Dihydrated sulphuric acid $\text{SO}_3, 2\text{H}_2\text{O}$. A liquid forming crystals at low temperatures which melt at 8° . Basic lead sulphate Pb_2SO_5 is a salt corresponding to this acid.

Trihydrated sulphuric acid $\text{SO}_3, 3\text{H}_2\text{O}$, the hydrate in the formation of which the maximum amount of contraction takes place, and which is represented by the salt, mercury orthosulphate (Turpeth mineral) Hg_3SO_6 .

The existence of numerous hydrates in addition to those above mentioned has been inferred by Pickering (*Chem. Soc. Trans.* 1890, 648, 331) from the study of various physical phenomena connected with acids of different strengths. One of these $\text{SO}_3, 5\text{H}_2\text{O}$ has been isolated in hard, well-defined crystals melting at -25° , whereas mixtures containing either more or less water (within certain limits) melt at lower temperatures. The work of Pickering has been extended and confirmed by Giran (*Bull. Soc. Chim.* 1913, 1049). He describes a hydrate $\text{H}_2\text{SO}_4, 2\text{H}_2\text{O}$, and notes the existence of eutectic points at -46° (67.5 p.c. H_2SO_4) and at -41° (75 p.c. H_2SO_4). The curve representing the solidifying points of mixtures of water with SO_3 beyond H_2SO_4 shows a maximum at $+35^\circ$ ($\text{H}_2\text{S}_2\text{O}_7$), and a change of direction at 26° ($\text{H}_2\text{S}_4\text{O}_{13}$). The curve terminates in a straight

line at the melting-point of pure βSO_3 (see also Donk, Chem. Weekblad. 1914, 956).

For the determination of sulphur dioxide in technical sulphuric acid, see Ditz and Kanhauser (Zeitsch. anal. Chem. 1924, 64, 28; J. Soc. Chem. Ind. 1924, 43, B, 630).

PHYSICAL PROPERTIES OF SULPHURIC ACIDS.

Commercially, sulphuric acids may be divided into two classes, viz. 'fuming acids' or substances indicated by the formula $m\cdot\text{SO}_3\cdot n\text{H}_2\text{O}$ where $m > n$; and 'non-fuming acids' where $m < n$ varying from O.V. (oil of vitriol), where m very nearly equals n , down to 'chamber acids' of sp.gr. 1.5 and less. The weaker acids on heating lose water, becoming more and more concentrated until finally a product is obtained boiling and distilling at above 300° , and containing between 98 and 99 p.c. H_2SO_4 , the remainder being water. Monohydrated acid 100 p.c. H_2SO_4 cannot be obtained in this way, but is readily formed by the addition of the appropriate amount of sulphur trioxide; the monohydrated acid cannot be distilled unchanged, as, on heating, the boiling-point rises from 290° to 338° , a mixture of $\text{H}_2\text{SO}_4\cdot\text{SO}_3$ and water passing over. It may also be obtained from 98 p.c. acid by cooling it to below 0° , and separating the crystals which form about that temperature, melting them and recrystallising. At ordinary temperatures it is a colourless oily liquid. Its sp.gr. is 1.8385 at 15° (Lunge and Nacfi), and the addition of a little SO_3 or water raises the sp.gr. It fumes slightly in air, even at ordinary temperatures giving off SO_3 , and it is completely dissociated into SO_3 and H_2O at about 440° (Deville and Troost).

NON-FUMING OR ORDINARY SULPHURIC ACIDS

Pictet (Compt. rend. 1894, 119, 642) gives a more complete table of freezing-points, and Knietzsch (Ber. 34, 4069), in his tables of the properties of sulphuric acid, gives a still more extended list.

PICTET'S TABLE.

Formula	H_2SO_4 per cent.	Sp.gr.	Fr.pt.
H_2SO_4	100.00	1842	$+10^\circ\text{C}$.
$\text{H}_2\text{SO}_4 + \text{H}_2\text{O}$	84.48	1777	$+3^\circ\text{C}$.
„ $+2\text{H}_2\text{O}$	73.08	1650	-70°C .
„ $4\text{H}_2\text{O}$	57.65	1476	-40°C .
„ $6\text{H}_2\text{O}$	47.57	1376	-50°C .
„ $8\text{H}_2\text{O}$	40.50	1311	-65°C .
„ $10\text{H}_2\text{O}$	35.25	1268	-88°C .
„ $11\text{H}_2\text{O}$	33.11	1249	-75°C .
„ $12\text{H}_2\text{O}$	31.21	1233	-55°C .
„ $13\text{H}_2\text{O}$	29.52	1219	-45°C .
„ $14\text{H}_2\text{O}$	28.00	1207	-40°C .
„ $15\text{H}_2\text{O}$	26.63	1196	-34°C .
„ $16\text{H}_2\text{O}$	25.39	1187	-26.5°C .
„ $18\text{H}_2\text{O}$	23.22	1170	-19°C .
„ $20\text{H}_2\text{O}$	21.40	1157	-17°C .
„ $25\text{H}_2\text{O}$	17.88	1129	-8.5°C .
„ $50\text{H}_2\text{O}$	9.82	1067	-3.5°C .
„ $75\text{H}_2\text{O}$	6.77	1045	-0°C .
„ $100\text{H}_2\text{O}$	5.16	1032	$+2.5^\circ\text{C}$.
„ $300\text{H}_2\text{O}$	1.78	1007	$+4.5^\circ\text{C}$.
„ $1000\text{H}_2\text{O}$	0.54	1001	$+0.5^\circ\text{C}$.

KNIETZSCH'S TABLE.

P.c. SO_3	Melting-point	P.c. SO_3	Melting-point
1	-0.6°C .	65	-4.2°C .
3	-1.7	66	$+1.2$
5	-2.7	67	$+8.0$
7	-4.4	68	$+8.0$
9	-6.0	69	$+7.0$
11	-7.2	70	$+4.0$
13	-8.2	71	-1.0
15	-9.3	72	-7.2
17	-11.4	73	-16.2
19	-15.2	74	-25
21	-22.5	75	-34
23	-40.1	76	-32
—	below -40	77	-28.2
61	-40	78	-16.5
62	-20	79	-5.2
63	-11.5	80	$+3$
64	-4.8	80.63	$+10$

The following table of the freezing- and melting- and boiling-points is compiled from the results obtained by Lunge (Ber. 1878, 370; and 1881, 2649; Technical Chemists' Handbook, 132):

Per cent. H_2SO_4	Sp.gr.	Boiling-point	Freezing-point	Melting-point
5	1.031	101°	—	—
10	1.069	102	—	—
15	1.107	103.5	—	—
20	1.147	105	—	—
25	1.184	106.5	—	—
30	1.224	108	—	—
35	1.265	110	—	—
40	1.307	114	—	—
45	1.352	118.5	—	—
50	1.399	124	—	—
53	1.428	128.5	—	—
56	1.459	133	—	—
60	1.503	141.5	—	—
62.5	1.530	147	—	—
65	1.557	153.5	—	—
67.5	1.585	161	—	—
70	1.615	170	—	—
72	1.639	174.5	—	—
74	1.661	180.5	Liquid at -20°	—
76	1.688	189	Do.	—
78	1.710	199	Do.	—
79.5	1.727	—	-7.5	-7.5
80	1.733	207	-8.5	-8.5
81.3	1.749	—	-0.2	$+4.5$
82	1.758	218.5	—	—
83.2	1.767	—	$+1.6$	$+6.5$
84	1.773	227	$+8.5$	$+8.5$
86	1.791	238.5	$+4.5$	$+8.0$
88	1.807	251.5	-9.0	-6.0
90	1.818	262.5	—	—
91	1.824	268	Liquid at -20	—
92	1.830	274.5	—	—
93	1.834	281.5	—	—
94	1.837	288.5	—	—
95	1.840	295	Liquid at -20	—

The specific gravity of dilute sulphuric acid of various degrees of concentration and at various temperatures has been examined by a number

SPECIFIC GRAVITY OF SULPHURIC ACID.

At 60°F. = 15.5°C.		100 parts by weight contain		1 litre contains kilos. of H ₂ SO ₄	At 60°F. = 15.5°C.		100 parts by weight contain		1 litre contains kilos. of H ₂ SO ₄
Sp.gr.	Degrees Twaddell	SO ₃	H ₂ SO ₄		Sp.gr.	Degrees Twaddell	SO ₃	H ₂ SO ₄	
1.20	40	22.30	27.32	0.328	1.67	134	60.95	74.66	1.246
1.21	42	23.33	28.58	0.346	1.68	136	61.63	75.50	1.268
1.22	44	24.36	29.84	0.364	1.69	138	62.29	76.30	1.289
1.23	46	25.39	31.11	0.382	1.70	140	63.00	77.17	1.312
1.24	48	26.35	32.28	0.400	1.72	142	63.70	78.04	1.334
1.25	50	27.29	33.43	0.418	1.72	144	64.43	78.92	1.357
1.26	52	28.22	34.57	0.435	1.73	146	65.14	79.80	1.381
1.27	54	29.15	35.71	0.454	1.74	148	65.86	80.68	1.404
1.28	56	30.10	36.87	0.472	1.75	150	66.58	81.56	1.427
1.29	58	31.04	38.03	0.490	1.76	152	67.30	82.44	1.451
1.30	60	31.99	39.19	0.510	1.77	154	68.17	83.41	1.478
1.31	62	32.94	40.35	0.529	1.78	156	68.98	84.50	1.504
1.32	64	33.88	41.50	0.548	1.79	158	69.96	85.70	1.534
1.33	66	34.80	42.66	0.567	1.80	160	70.96	86.92	1.565
1.34	68	35.71	43.74	0.586	1.805	161	71.50	87.60	1.581
1.35	70	36.58	44.82	0.605	1.81	162	72.08	88.30	1.598
1.36	72	37.45	45.88	0.624	1.815	163	72.69	89.05	1.621
1.37	74	38.32	46.94	0.643	1.820	164	73.51	90.05	1.639
1.38	76	39.18	48.00	0.662	1.821		73.63	90.20	1.643
1.39	78	40.05	49.06	0.682	1.822		73.80	90.40	1.647
1.40	80	40.91	50.11	0.702	1.823		73.96	90.60	1.651
1.41	82	41.76	51.15	0.721	1.824		74.12	90.80	1.656
1.42	84	42.57	52.15	0.740	1.825	165	74.29	91.00	1.661
1.43	86	43.36	53.11	0.759	1.826		74.49	91.25	1.666
1.44	88	44.14	54.07	0.779	1.827		74.69	91.50	1.671
1.45	90	44.92	55.03	0.798	1.828		74.86	91.70	1.676
1.46	92	45.69	55.97	0.817	1.829		75.03	91.90	1.681
1.47	94	46.45	56.90	0.837	1.830	166	75.19	92.10	1.685
1.48	96	47.21	57.83	0.856	1.831		75.46	92.43	1.692
1.49	98	47.95	58.74	0.876	1.832		75.69	92.70	1.698
1.50	100	48.73	59.70	0.896	1.833		75.89	92.97	1.704
1.51	102	49.51	60.65	0.916	1.834		76.12	93.25	1.710
1.52	104	50.28	61.59	0.936	1.835	167	76.35	93.56	1.717
1.53	106	51.04	62.53	0.957	1.836		76.57	93.80	1.722
1.54	108	51.78	63.43	0.977	1.837		76.90	94.20	1.730
1.55	110	52.46	64.26	0.996	1.838		77.23	94.60	1.739
1.56	112	53.22	65.20	1.017	1.839		77.55	95.00	1.748
1.57	114	53.95	66.09	1.038	1.840	168	78.04	95.60	1.759
1.58	116	54.65	66.95	1.058	1.8405		78.33	95.95	1.765
1.59	118	55.37	67.83	1.078	1.8410		78.69	96.30	1.784
1.60	120	56.09	68.70	1.099	1.8415		79.47	97.35	1.792
1.61	122	56.79	69.06	1.120	1.8410		80.16	98.20	1.808
1.62	124	57.49	70.42	1.141	1.8405		80.43	98.52	1.814
1.63	126	58.18	71.27	1.162	1.8400		80.59	98.72	1.816
1.64	128	58.88	72.12	1.182	1.8395		80.63	98.77	1.817
1.65	130	59.57	72.96	1.204	1.8390		80.93	99.12	1.823
1.66	132	60.26	73.81	1.225	1.8385		81.08	99.31	1.826

of chemists and physicists with results not always exhibiting as close concordance as might be desired ; the earlier tables given by Vauquelin d'Arcet, Ure, Parkes, &c., have long been regarded as superseded by the more exact ones of Bineau and Kolb ; and these have been further corrected as a result of the investigations of Lunge, Isler, and Naef. Ure's table, although incorrect, is still largely used as a standard for commercial purposes. For acids approaching the concentration of O.V. the sp.gr. is a fallacious test of strength, because acid of strength 98 p.c. H₂SO₄ has a maximum density as compared with either stronger or weaker acid.

Apart from this, the effect of temperature variation in altering the sp.gr. is greater, whilst the effect of a given increment in strength is less,

the stronger the acid. The table given above is taken from Lunge's Technical Chemist's Handbook,¹ and is based on the latest results of the above-mentioned investigators with some corrections introduced by the Imperial German Standards Commission.

S. U. Pickering has published (Chem. Soc. Trans. 1890, 64) a number of observations on the sp.gr. of sulphuric acid of strengths between 0.997007 and 99.85700 p.c. of H₂SO₄, in which it is claimed that the limit of error does not, as a rule, exceed 0.000008 (eight parts in one million), notwithstanding that the eight determinations of the strength of the strong sulphuric acid used to prepare other strengths by dilution

¹ The latest edition of what was previously known as the Alkali-Makers' Handbook.

varied between 99·704 and 99·962 p.c., showing a range of 0·258, or about 1 part in 400. Founded on these results, H. D. Richmond has calculated a table (J. Soc. Chem. Ind. 1890, 479) of specific gravities of sulphuric acid between the limits 1·8248 and 1·8384 referred to water at 15° (90·86–100 p.c.).

Another table, ‘the result of a careful selection of figures from standard authorities,’ has been calculated by A. H. Elliott (The Chemical

Trade Journal, March 24, 1888, 182). W. C. Ferguson (J. Soc. Chem. Ind. 1905, 781) gave the table adopted by the Manufacturing Chemists Association of the United States.

The specific gravity of commercial sulphuric acid, as compared with its strength, usually differs slightly from that found in the case of chemically pure acid, owing to the presence of lead sulphate and other impurities.

VARIATION OF SPECIFIC GRAVITY WITH TEMPERATURE.

0°	10°	20°	30°	40°	50°	75°	100°
1·857	1·846	1·835	1·825	1·816	1·806	1·782	1·762
1·807	1·796	1·784	1·773	1·762	1·751	1·725	1·700
1·754	1·745	1·735	1·726	1·716	1·706	1·683	1·660
1·704	1·695	1·685	1·676	1·666	1·656	1·634	1·610
1·654	1·645	1·635	1·626	1·617	1·608	1·586	1·565
1·604	1·595	1·585	1·576	1·567	1·558	1·537	1·516
1·552	1·544	1·536	1·528	1·520	1·512	1·491	1·469
1·502	1·494	1·486	1·478	1·470	1·462	1·441	1·419
1·452	1·444	1·436	1·429	1·423	1·416	1·395	1·374
1·402	1·394	1·386	1·379	1·372	1·364	—	—
1·352	1·344	1·336	1·330	1·324	1·316	—	—
1·300	1·293	1·287	1·280	1·274	1·267	—	—
1·250	1·243	1·237	1·230	1·224	1·217	—	—
1·200	1·193	1·186	1·180	1·173	1·165	—	—
1·149	1·143	1·137	1·131	1·125	1·119	—	—
1·098	1·093	1·087	1·082	1·077	1·072	—	—
1·048	1·043	1·037	1·032	1·028	1·022	—	—

Specific heat of dilute sulphuric acid.—F. Bode gives the following table indicating the relationship between the sp.gr. at 15°, and the specific heat of sulphuric acid (Zeitsch. angew. Chem. 1889, 244; also J. Soc. Chem. Ind. 1889, 543):—

SPECIFIC HEAT OF SULPHURIC ACID.

Specific gravity	Degrees Baumé	Specific heat	Specific gravity	Degrees Baumé	Specific heat
1·842	66	0·3315	1·320	35	0·67
1·774	63	0·38	1·263	30	0·73
1·711	60	0·41	1·210	25	0·78
1·615	55	0·45	1·162	20	0·82
1·530	50	0·49	1·116	15	0·87
1·453	45	0·55	1·075	10	0·90
1·383	40	0·60	1·037	5	0·95

A number of determinations of the heat capacity of sulphuric acid solutions of different strengths have also been recorded by S. U. Pickering (Chem. Soc. Trans. 1890, 64). The thermal properties of sulphuric acid and oleum have been investigated by Porter (Trans. Faraday Soc. 1917).

For the specific heat of sulphuric acid, nitric acids, and their mixtures, see Pascal and Garnier (Soc. Chim. Bull. Jan. 5, 1920, [iv.] 27–28, pp. 8–18). As the dilution with water of the sulphuric acid increased from 0 to 90 p.c. the specific heat goes up from 0·335 to 0·916; the specific heat of nitric acid with 98·15 p.c. of HNO₃ is 0·475, that of the 10 p.c. acid 0·900—all values reduced to 20°. A mixture of 22 p.c. sulphuric acid, 77 nitric, and 0·7 NO₂ has a specific heat of 0·430; when the proportions are 90, 9·9, 0·1, the heat is 0·3444 (Science Abstracts, 1923, 289, p. 53).

The results of determinations by Pascal and Garnier (Mém. poudres, 1923, 20, 29) of the specific heats of sulphuric acid, nitric acid and their mixtures are well shown by plotting on a ternary diagram. These observers have also carried out a very extensive series of distillations of mixtures of nitric and sulphuric acids.

Tension of aqueous vapour emitted by dilute sulphuric acid.—E. Sorel has made a number of experiments, leading to the following results, abridged from much fuller tables (Bull. Soc. Ind.

Percentage of H ₂ SO ₄ in acid	Temperature								
	10°	20°	30°	40°	50°	60°	70°	80°	90°
44	4·4	8·5	15·5	28·1	48·3	—	—	—	—
48	3·7	7·1	13·4	23·9	40·1	69·0	107·2	—	—
52	3·0	5·8	10·9	18·9	31·5	54·0	84·5	131·2	207·9
56	2·2	4·3	8·1	14·2	24·1	41·6	65·0	100·9	160·0
60	1·6	3·0	6·1	10·0	16·9	28·7	46·1	72·3	118·7
64	1·2	2·2	4·0	6·5	10·9	18·7	30·3	48·0	83·7
68	0·9	1·5	3·0	4·5	7·2	12·3	19·4	31·4	56·0
72	0·7	1·0	2·0	3·2	4·8	7·5	12·0	20·0	33·7
76	0·4	0·5	1·4	2·1	3·0	4·8	7·5	11·8	18·5
80	0·2	0·3	0·8	1·3	1·9	2·9	4·1	6·2	9·3

Mulhouse, 1890, 240; also J. Soc. Chem. Ind. 1890, 175). The figures represent tensions in millimetres of mercury; obviously they are much below the tensions of aqueous vapour in contact with water (Hacker, Ann. Physik. 1912, 1338; also Hartung, Trans. Farad. Soc. 1920, 15, 3, 150; cf. Thomas and Ramsay, J. Chem. Soc. Trans. 1923, 123, 3256).

The earliest determinations of the viscosity of mixtures of sulphuric acid and water seem to be those of Graham (Trans. Roy. Soc. Lond. 1861, 157A, 373) and whose measurements were taken at 20°C. Wagner (Ann. Physik. 1883, 18, 259), using only three mixtures, containing respectively 23.4, 15.5, and 7.87 p.c. of sulphuric acid, gives the viscosities at 15°, 25°, 35° and 45°C.

The viscosity of sulphuric acid has been also studied by Dunstan and Wilson (Jour. Chem. Soc. 1907, 85; Proc. Chem. Soc. 1914, 104), Kremann and Erlich (Monatsh. 1915, 831), also Smits and others (Proc. Ac. Sci. Amsterdam, 1921, 23, 969), Jorinson (Rec. trav. chim. 1921, 40, 281). The surface tension has been determined by Morgan and Davis (J. Amer. Chem. Soc. 1916, 555) and the existence of numerous hydrates rendered probable. Enklaar (Zeitch. Physikal. Chem. 80, 616) records the neutralisation and dissociation constants of sulphuric acid of varying concentrations (also Müller, Bull. Soc. Chim. 13, 1053).

Rhodes and Barbour (Ind. Eng. Chem. 1923, 15, 850) obtained viscosity curves of a similar general form to those of Dunstan and Wilson, showing maxima at 84.5 and 100 p.c. sulphuric acid corresponding to $\text{H}_2\text{SO}_4\text{H}_2\text{O}$ and H_2SO_4 respectively, also a minimum at 94.5 p.c. The figures obtained are, however, very much lower than those found by Dunstan and Wilson. The maxima and minima are less pronounced at 75° than at lower temperatures, probably indicating the dissociation at higher temperatures of hydrate complexes. These viscosities are not only of general scientific interest, but are also of value in calculating the rates of flow in pipes when using the modified Fanning formula, given by Wilson, McAdams and Seltzer (Ind. Eng. Chem. 1922, 14, 105).

Stone (Ind. Eng. Chem. 1923, 15, 977) shows that by employing the correction made by Dunstan to the values obtained by Dunstan and Wilson, there is closer agreement with the results obtained by Rhodes and Barbour.

Tension of nitrous anhydride dissolved in sulphuric acid at different temperatures.—E. Sorel (*l.c. supra*) has made a number of determinations of the amounts of nitrous anhydride given off when sulphuric acid of different strengths, and containing different proportions of dissolved nitrous gases, was made to flow through a spiral tube 5 metres long placed in a water-bath at constant temperature, whilst a current of pure nitrogen gas passed through the spiral in the opposite direction; the results obtained varied from 0.009 milligram of N_2O_3 per litre of nitrogen at 0° and 760 mm., when acid of sp.gr. 1.774, containing 28.4 grms. N_2O_3 per litre, was passed through at 40.1°, up to 109.15 milligrams, when acid of sp.gr. 1.597, containing 12.5 grms. N_2O_3 per litre, was passed through at 89.9°; in general, the weaker the acid and the higher the temperature the more N_2O_3 was evolved.

G. Lunge (Zeitsch. angew. Chem. 1891, 37; also J. Soc. Chem. Ind. 1891, 364) has carried out a large number of farther observations on this point, employing substantially the same method with the difference that carbon dioxide was used instead of nitrogen, and a 10-bulbed tube instead of a spiral. Pure nitrosulphonic acid dissolved in pure sulphuric acid was used; no nitric acid was found in the solution. The following tables, representing grms. per litre throughout, are abridged from those given for nitrous vitriol of gravity respectively 1.720, 1.686, 1.633, and 1.60, and for temperatures of 50°–90°. When plotted as curves, the figures show that in presence of strong acid, and at low temperatures, nitrosulphonic acid exists as a compound in the fluid; but, on diluting the liquid and raising the temperature, the compound is dissociated, and the nitrous acid formed removed by the gases into which it diffuses.

LOSS OF N_2O_3 AFTER 1 HOUR, DURING WHICH TIME 5 LITRES OF CO_2 WERE PASSED.

Originally present	50°	60°	70°	80°	90°
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Nitrous vitriol, sp.gr. 1.72=78 p.c. H_2SO_4 .

1	—	—	—	—	0.006
5	—	—	—	—	0.037
10	—	—	—	0.018	0.093
15	—	—	0.006	0.056	0.193
20	—	—	0.031	0.150	0.356
25	0.012	0.031	0.125	0.312	0.600
30	0.081	0.125	0.293	0.550	0.956
35	0.156	0.312	0.525	0.868	1.375
40	0.268	0.500	0.775	1.193	1.800
45	0.406	0.712	1.050	1.537	2.337
50	0.550	0.931	1.325	1.875	2.675

Nitrous vitriol, sp.gr. 1.686=76 p.c. H_2SO_4 .

8	—	—	—	—	0.025
10	—	—	—	0.012	0.050
15	—	—	0.025	0.100	0.225
20	—	0.050	0.186	0.425	0.625
25	0.010	0.200	0.462	1.025	1.662
30	0.062	0.362	0.750	1.700	2.812
35	0.275	0.625	1.250	2.362	4.175
40	0.486	0.886	1.736	3.025	5.550
45	0.825	1.300	2.325	3.736	6.975
49	1.100	1.650	2.886	4.236	8.100

Nitrous vitriol, sp.gr. 1.633=71½ p.c. H_2SO_4 .

1	0.012	0.025	0.036	0.100	0.150
5	0.212	0.300	0.436	0.736	0.825
10	0.700	0.936	1.436	2.086	2.375
15	1.186	1.675	2.412	3.450	4.162
20	1.662	2.412	3.400	4.850	5.986
25	2.700	3.636	5.000	6.800	8.662
30	4.412	5.412	7.350	9.675	13.125
32	5.236	6.325	8.575	11.175	16.362

Nitrous vitriol, sp.gr. 1.60=69 p.c. H_2SO_4 .

1	0.050	0.086	0.175	0.336	0.412
5	0.812	1.150	1.500	2.120	2.700
10	1.975	2.812	3.712	4.990	6.475
15	3.360	4.612	6.125	8.400	10.625
20	4.700	6.425	8.562	11.850	14.800

Heat of solution of sulphuric acid.—A considerable amount of heat is evolved on mixing sulphuric acid with water. Knietzsch (Ber. 1901,

4103) gives the following table for the heats of solution of acids of different strengths.

SO ₃ p.c.	H ₂ SO ₄ p.c.	Cal- ories	SO ₃ p.c.	H ₂ SO ₄ p.c.	Cal- ories
50	61.25	39	67	82.08	93
51	62.48	41	68	83.30	98
52	63.70	44	69	84.53	103
53	64.93	46.5	70	85.75	108
54	66.15	49	71	86.98	113
55	67.38	51.5	72	88.20	119
56	68.60	54	73	89.43	126
57	69.83	57	74	90.65	133
58	71.05	59.5	75	91.88	139
59	72.28	62	76	93.10	146
60	73.50	65	77	94.33	152
61	74.73	68	78	95.55	160
62	75.95	72	79	96.78	168
63	77.18	75	80	98.00	178
64	78.40	79	81	99.23	188
65	79.63	83.5	81.63	100.00	193
66	80.85	88			

FUMING SULPHURIC ACIDS.

Fuming acid is generally valued in proportion to the amount of trioxide present, the balance being H₂SO₄. The sp.gr. is sometimes employed as a test of strength, but is fallacious, since the density of acid containing about 60 p.c. of SO₃ is a maximum, both stronger and weaker acids exhibiting lower densities. The following table is given by R. Messel (J. Soc. Chem. Ind. 1885, 573), all the specimens being liquid at 26.6°:—

Physical character at 60°F.	Percentage of SO ₃	Specific gravity	
		At 80°F. =26.6°C.	Calculated to 60°F. =15.5°C.
—	8.3	1.842	1.852
Liquid .	30.0	1.930	1.940
Crystalline	40.0	1.956	1.970
mass resem- }	44.5	1.961	1.975
bling nitre . }	46.2	1.963	1.977
—	59.4	1.980	1.994
Liquid .	60.8	1.992	2.006
	65.0	1.992	2.006
	69.4	2.002	2.016
Crystalline .	72.8	1.984	1.998
	80.0	1.959	1.973
	82.0	1.953	1.967

C. Winkler has obtained values slightly differing from Messel's, the acid used being 'commercial,' and therefore possibly not quite pure.

Specific gravity at 20°C.	Per- centage of SO ₃	Specific gravity at 20°C.	Per- centage of SO ₃
1.860	1.54	1.920	15.95
1.870	4.28	1.930	21.34
1.880	6.42	1.940	28.03
1.890	8.16	1.950	31.46
1.900	10.07	1.960	35.87
1.910	11.43	1.970	44.64

Knietsch (Ber. 1901, 4101) gives a more complete table of sp.grs. at 35°, also for com-

mercial fuming acid, and in addition a series of observations at 15° and 45°. He finds that acid containing 60 p.c. free SO₃ has the maximum density at 15°, 56 p.c. free SO₃ at 35°, and 50 p.c. free SO₃ at 45°.

SPECIFIC GRAVITIES OF FUMING ACID AT 35°C.

Free SO ₃ p.c.	Sp.gr.	Free SO ₃ p.c.	Sp.gr.	Free SO ₃ p.c.	Sp.gr.
0	1.8186	34	1.9405	68	1.9600
2	1.8270	36	1.9474	70	1.9564
4	1.8360	38	1.9534	72	1.9502
6	1.8425	40	1.9584	74	1.9442
8	1.8498	42	1.9612	76	1.9379
10	1.8565	44	1.9643	78	1.9315
12	1.8627	46	1.9672	80	1.9251
14	1.8692	48	1.9702	82	1.9183
16	1.8756	50	1.9733	84	1.9115
18	1.8830	52	1.9749	86	1.9046
20	1.8919	54	1.9760	88	1.8980
22	1.9020	56	1.9772	90	1.8888
24	1.9092	58	1.9754	92	1.8800
26	1.9158	60	1.9738	94	1.8712
28	1.9220	62	1.9709	96	1.8605
30	1.9280	64	1.9672	98	1.8488
32	1.9338	66	1.9636	100	1.8370

A more accurate method consists in weighing out a portion of the acid to be examined in a sealed bulb, which is then broken under water by shaking up in a bottle; sulphurous acid, generally present, is first determined by titration with iodine solution, and then the SO₃ by precipitation as barium sulphate or volumetrically (Messel, *l.c.* p. 521). Lunge and Rey (Zeitsch. angew. Chem. 1891, 163) recommend a special form of bulb-tap pipette instead of a sealed bulb for this purpose. The table on p. 560 is abridged from a longer one given by Lunge and Hurter (Technical Chemists' Handbook, p. 134), for the reduction of percentages of total SO₃ thus found to percentages of SO₃, the balance being H₂SO₄.

Setlik finds (Chem. Zeit. 13, 1760; Chem. Soc. Abstr. 1890, 414; J. Soc. Chem. Ind. 1890, 417) that a simple method of valuation, with sufficient accuracy for most purposes, is to titrate 100 grms. in a flask with water until the acid ceases to give off fumes, the flask being kept cool. At first a thick cloud is formed on the addition of each drop, but latterly the fumes become less apparent. The flask must then be shaken after each addition of water until the fumes are absorbed before adding the next portion: 1 c.c. of water represents 4.444 grms. SO₃. Acids containing more than 35 p.c. of SO₃ should be diluted down to about that strength by addition of pure H₂SO₄. Lunge regards this method as insufficiently accurate for use between buyer and seller, although otherwise convenient. For the apparatus for the analysis of oleum and other fuming liquids, see Bosshard (Helv. Chim. Acta, 1924, 7, 330; Analyst. 1924, 49, 301).

It may, however, be rendered quite reliable for practical purposes by using sulphuric acid of known strength instead of water.

Melting- and boiling-points of fuming acids.
—The following tables are given by Knietsch (Ber. 1901, 4100 and 4101).

The numbers in the brackets denote the fusing-points of fresh not yet polymerised acids.

Total SO ₃ found by analysis	Contains per cent.	
	SO ₄ H ₂	SO ₃
81.63	100	0
82.00	98	2
82.37	96	4
82.73	94	6
83.10	92	8
83.47	90	10
83.84	88	12
84.20	86	14
84.57	84	16
84.94	82	18
85.31	80	20
85.67	78	22
86.04	76	24
86.41	74	26
86.78	72	28
87.14	70	30
87.51	68	32
87.88	66	34
88.24	64	36
88.61	62	38
88.98	60	40
89.35	58	42
89.71	56	44
90.08	54	46
90.45	52	48
90.82	50	50
91.18	48	52
91.55	46	54
91.92	44	56
92.29	42	58
92.65	40	60
93.02	38	62
93.39	36	64
93.76	34	66
94.12	32	68
94.49	30	70
94.86	28	72
95.22	26	74
95.59	24	76
95.96	22	78
96.33	20	80
96.69	18	82
97.06	16	84
97.43	14	86
97.80	12	88
98.16	10	90
98.53	8	92
98.90	6	94
99.27	4	96
99.73	2	98
100.00	0	100

Sulphur trioxide, or sulphuric anhydride, when quite pure and free from traces of water is a crystalline solid melting at 14.8° to a colourless liquid which boils at 46.2° (Weber, Ber. 19, 3187). The crystals are long transparent prisms similar to those of potassium nitrate. The presence of a trace of water renders this form

unstable, and on standing for some time it changes to an asbestos-like solid which begins to melt at about 50°, gradually passing back to the original form. Oddo (Chem. Zentr. 1901,

Total SO ₃ per cent.	Free SO ₃ per cent.	Boiling-point
82.3	3.64	212°
83.4	9.63	170
86.45	26.23	125
89.5	42.84	92
93.24	63.20	60
99.5	97.2	43

Free SO ₃ per cent.	Melting-point	Free SO ₃ per cent.	Melting-point
0	+10.0°	55	+18.4°
5	+3.5	60	+0.7
10	−4.8	65	+0.8
15	−11.2	70	+9.0
20	−11.0	75	+17.2
25	−0.6	80	+22.0
30	+15.2	85	+33.0 (27)
35	+26.0	90	+34.0 (25)
40	+33.8	95	+36.0 (26)
45	+34.8	100	+40.0 (17.7)
50	+28.5		

969) showed that the second modification was a polymer of the first, and should be represented by the formula S₂O₆. Schenck (Annalen, 316, 1) regards the more liquid modification as a solution of the asbestos-like polymer in real SO₃ in a state of unstable equilibrium. Knietsch (Ber. 1901, 4100) gives the melting-point of pure SO₃ as 17.7°. On adding small quantities of water the melting-point is raised until at 85 p.c.

SPECIFIC HEATS OF FUMING ACIDS (Knietsch).

Total SO ₃ p.c.	Free SO ₃ p.c.	Sp.heat
76.4	—	0.3691
81.5	—	0.3478
83.46	10	0.3417
85.48	20.95	0.3391 (min.)
90.0	45.56	0.360
93	61.89	0.425
94.64	70.6	0.473
97	83.67	0.590
99	94.06	0.710
100	100.0	0.770

free SO₃ it is 27° (maximum). On standing this polymerises; it no longer melts on heating, but sublimes and passes back again to the original modification.

Berthoud (Helv. Chim. Acta, 1922, 5, 513) determined the physical constants of both forms of sulphur trioxide. He kept the two forms in contact with each other for four years. The relative amounts of the two forms remained constant. When a sealed flask containing the β form was heated, fusion began at 55° and the

amount of liquid increased at this temperature for about 24 hours and then remained constant

HEATS OF SOLUTION OF FUMING ACIDS
(Knietsch).

SO ₃ total per cent.	SO ₃ free per cent.	Calories	Heat of solu- tion of solid acids
82	2.0	199	—
83	7.5	210	—
84	12.9	223.5	—
85	18.3	237.5	—
86	23.5	250	—
87	29.2	265	—
88	34.7	278	—
89	40.1	292	—
90	45.6	308	286
91	51.0	325	304
92	56.4	344	322
93	61.9	363	340
94	67.3	381	360
95	72.8	401	380
96	78.3	421	402
97	83.7	442	423
98	89.1	465	442
99	84.6	490	463
100	100.0	515	486

for several days. When the temperature was raised to 68° more liquid was formed and a new equilibrium was established. Complete fusion

occurred at 80° to 90°. He concludes that the β form is not a simple modification of trioxide but very probably a product of hydration.

The results of about three years' investigations on the allotropic modifications of sulphur trioxide, are given by Smits and Schoenmaker in "The Complexities of the Solid State" (J. Chem. Soc. 1924, 125, 2554). The writers deal mainly with the *ice* form, which appears to be one of two metastable modifications, the other being a low melting *asbestos* form. The changes in the vapour pressure of the solid phase, and the corresponding changes in the melting ranges have been recorded. Further data relating to similar phenomena in the behaviour of the two *asbestos* forms are promised in a later article.

Knietsch also gives tables of electric resistance, vapour tensions, viscosities, capillarity, and action on iron, and he has plotted them out graphically in a series of curves representing the properties of sulphuric acid both fuming and ordinary (Fig. 1) (J. Soc. Chem. Ind. 1902, 343).

These curves show that the acid containing 98.3 p.c. H₂SO₄, which is the maximum strength obtainable on concentrating weaker acids by heat, and which distils unchanged, has certain well-defined properties. It has the maximum boiling-point and minimum vapour tension. It has the highest specific gravity of any hydrated acid. Electrical resistance begins suddenly to rise at this point to a maximum at 100 p.c. H₂SO₄, and the action of the acid on iron decreases at the same time to a minimum.

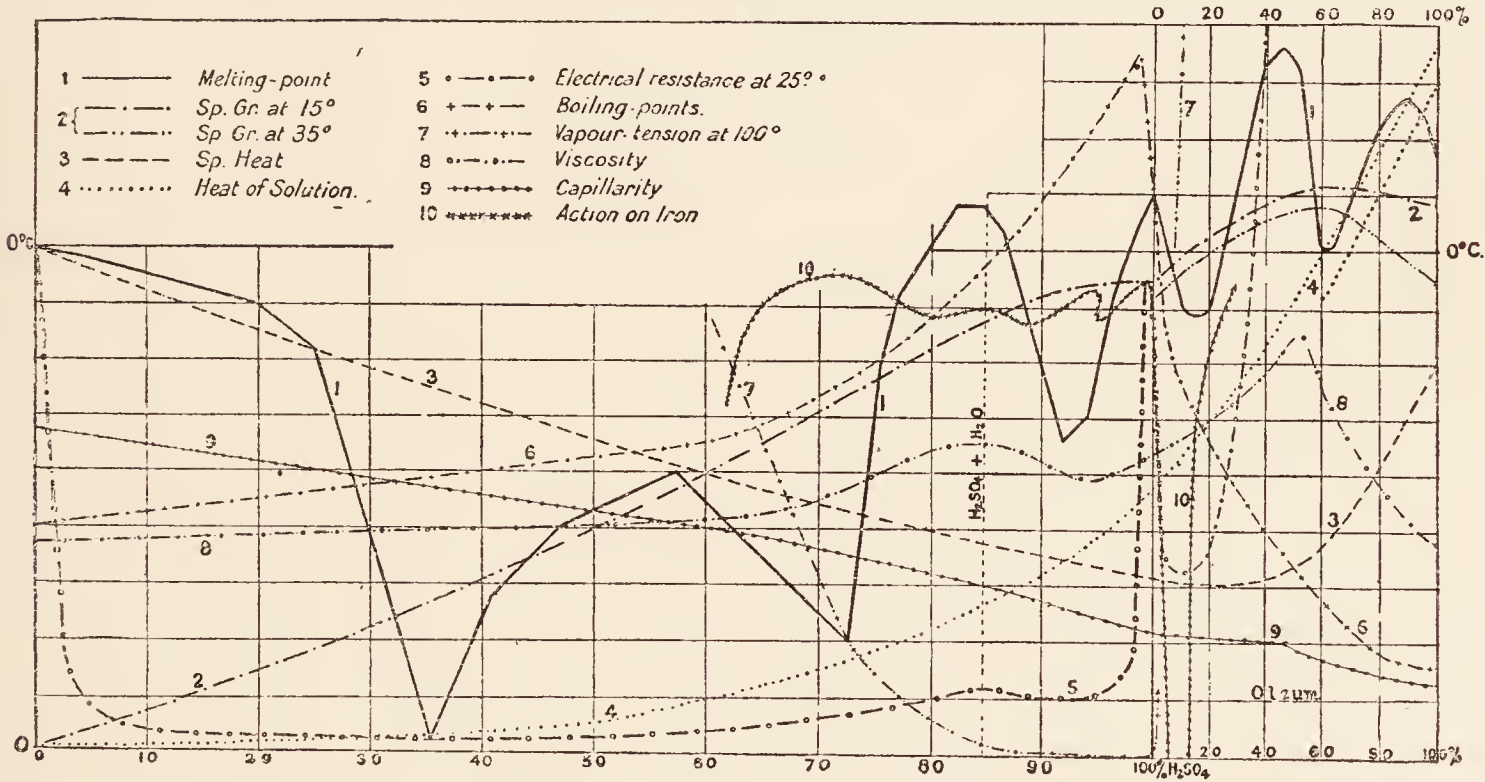


FIG. 1.

Other features of these curves to be noted are—

I. Melting-point. Shows sharply defined maxima and minima at points representing definite molecular proportions of H₂SO₄ to H₂O or to SO₃.

II. Density. Maxima at 98.3 p.c. H₂SO₄ and at 62 p.c. free SO₃.

III. Specific heat. Minimum at 20 p.c. free SO₃.

IV. Heat of solution. Rises steadily at increasing rate.

V. Electrical resistance. Great increase in conductivity caused by addition of a small quantity of acid to water. Indication of

hydrate H₂SO₄.H₂O by small maximum there. Enormously rapid increase of resistance as H₂SO₄ approached (maximum resistance), and correspondingly rapid decrease on addition of SO₃ to H₂SO₄ until 10 p.c. free SO₃ reached, from which point there is again a rapid increase.

VI. Boiling-point. Maximum 98.3 p.c. H₂SO₄.

VII. Action on iron. Read from top of diagram. Maximum action at 10 p.c. free SO₃.

The action of sulphuric acids, both fuming and ordinary, on iron and lead is a matter of considerable importance, as these metals are used to a large extent in the processes of manufacture of these acids.

Cast iron.—Acids of all strengths from chamber acid of 100°Tw. to 100 p.c. H_2SO_4 have very little action at ordinary temperatures, but if boiled in cast-iron vessels considerable action takes place with the weaker strengths, but it decreases as the acid becomes more concentrated, until at 98 p.c. H_2SO_4 the iron is scarcely attacked at all. Fuming acids below 20 p.c. free SO_3 have a somewhat greater action than 98–100 p.c. H_2SO_4 , but above that strength the action practically ceases; but cast-iron vessels are not suitable for the manufacture of fuming acids, owing to the fact that the SO_3 penetrates into the pores of the metal causing strains (probably due to the formation of gases in the pores by action on the carbon) which cause them to suddenly crack without any warning (see Rhead, *J. Soc. Chem. Ind.* 1918, 53 R; also Aitchison, *J. Chem. Soc.* 1916, 288).

On the other hand, wrought iron is unattacked by fuming acids above 27 p.c. free SO_3 , but below that strength some action takes place, it being greatest about 10 p.c. free SO_3 .

Wrought iron is acted on more rapidly than cast iron by acids below 100 p.c. H_2SO_4 , especially at high temperatures, but in the cold the action is very slight with acids above 120°Tw., and wrought-iron or steel vessels are very largely used for conveying and storing acids of all strengths above 70 p.c. H_2SO_4 .

Fawsitt and Powell (*J. Soc. Chem. Ind.* 1914, 33, 234) have studied the effect of temperature, quality of iron, and quality of acid on the rate of reaction. The safety of the carriage of sulphuric acid in iron drums depends on the quality of the acid, the size of the air-space left when filling, the temperature, and the time that elapses before the pressure is released. A further report by Fawsitt is given in *Chem. Age*, 1920, 2, 32.

Interesting observations upon the rate of solution of iron by sulphuric acid, both at rest and in motion, have been made by Friend and Dennett (*J. Chem. Soc.* 1922, 121, 41).

The effect of velocity on the corrosion of steel in sulphuric acid has been studied by Whitman and others (*Ind. Eng. Chem.* 1923, 15, 672). The net corrosion observed, being the sum of two effects, is chiefly determined by gaseous hydrogen evolution at very low velocities and by oxygen depolarisation at high velocities and passes through a minimum point in the intermediate ranges.

Alloys of iron and silicon are much less attacked by boiling acids than iron itself, and vessels made of certain of these alloys (metilure, tantiron, ironac, narki, &c.) may be used for concentrating even very weak acids up to 98 p.c. H_2SO_4 . Fuming acids, however, energetically attack these alloys.

Lead.—The action of acids up to 140°–150°Tw. is very slight even when heated to near the boiling-point of the acid, but if the latter is actually boiled the lead is strongly attacked. Above 150°Tw. up to 96 p.c. H_2SO_4 the action is still inconsiderable in the cold, but increases as the temperature rises, the lead being rapidly dissolved by ordinary concentrated sulphuric acid at about 250°–260°C. Monohydrate acts still more strongly, and fuming acids even at ordinary temperatures energetically attack this metal.

The solubility of lead sulphate in concentrated sulphuric acid has been determined by Ditz and Kannhauser (*Zeitsch. anorg. Chem.* 1916, 128). The solubility increases slowly to 97 p.c. acid, then rises rapidly to 100 p.c. where it reaches a maximum; the curve then falls to a percentage of trioxide about 5 p.c. followed by a rapid rise to 15 p.c. trioxide.

The solubility of lead sulphate in sulphuric acid of various concentrations and temperatures is given graphically by Frisak (*Metall. u. Erz.* 1922, 19, 200). An actual curve of lead present during concentration follows the experimental curves fairly closely. It is calculated that a pan using 3 tons of acid in 24 hours would lose 0.27 kg. of lead per day.

The impurities in ordinary lead have a considerable influence on its resistance to the action of sulphuric acid under different conditions. At ordinary temperatures, and even up to 100°C., the purest lead is least attacked by sulphuric acids concentrated or dilute. Impurities such as bismuth, antimony, zinc, or copper all have a harmful effect, but for very high temperatures approaching 200° as in the hottest concentrating pans the addition of a little copper (0.1–0.2 p.c.) appears to be of advantage (Lunge and Cumming, *Manufacture of Acids and Alkalis*, vol. i. 226, 1923). The influence of physical condition and chemical composition on commercial lead for pan concentration of sulphuric acid has also been investigated by Hart (*J. Soc. Chem. Ind.* 1907, 504).

Watson, Atwell and Fuwa (*J. Soc. Chem. Ind.* 1923, 251, T.; *J. Ind. Eng. Chem.* 1923, 15, 617) have investigated the production of sulphuric acid and caustic soda by the electrolysis of solutions of sodium sulphate. The results were not promising and seem to be of doubtful economic value even in regions where plentiful supplies of native sodium sulphate are available.

THE MANUFACTURE OF SULPHURIC ACID.

Two methods have been employed for the manufacture of sulphuric acid: (1) By decomposing natural or artificially prepared sulphates by heat, and (2) by burning sulphur or ores containing sulphur to sulphur dioxide, and further oxidising the latter to sulphur trioxide or sulphuric acid. Since about 1900 the first method has fallen into disuse, but before that time it had been employed for a great many years for making fuming acid, and it has been known for centuries, and was the original method by which sulphuric acid was first obtained.

The production of sulphuric acid from gypsum or by-product calcium sulphate has been attempted in Germany, and we understand that this method is not to be abandoned even when the abnormal conditions of pyrites importation, prevailing at the time of its introduction (1915), have been removed. The decomposition of the calcium sulphate is conducted solely by heat in a revolving tubular furnace similar to those employed in the production of cement clinker. The manufacture of sulphuric acid combined with production of cement has been suggested by Basset (*U.S. Pat.* 1197331, 1916). The utilisation of waste calcium sulphate from several

sources is certainly worth consideration (J. Soc. Chem. Ind. 1918, 378 R; also Tonindustrie Zeit. Sept. 3, 1918). The decomposition of sulphates by heating with clay and the utilisation of both gaseous and solid products is described by Cantilena (Ind. Chim. 14, 39), and in Swiss Pats. 72627, 1916; 74525, 1917; also Bambach, Eng. Pat. 3174, 1914.

The question of the preparation of sulphuric acid from the sulphates of the alkaline earths is discussed by Riesenfeld (J. pr. Chem. 1920, 100, 115). Further information will be found in J. Soc. Chem. Ind. 1919, 113 R, 352 R, and 378 R; and Annual Repts. 1920, 175.

Hutin (Mon. sci. 1923, 13, 254) mentions several methods of recovering sulphuric acid from gypsum. Feld's polythionate process is probably the most interesting, since it is reported that Germany replaced the importation of 300,000 tons pyrites per year by this means. The others include Helbig and Schaffner's and the Badische Co.'s suggestions.

During the last century, however, by far the larger quantity of acid has been obtained by the second method. If sulphur or materials containing sulphur are burnt in excess of air sulphur dioxide is produced, together with a little sulphur trioxide, and the oxidation of the sulphur dioxide is completed in one of two ways. 1. By the action of oxides or acids of nitrogen in the presence of steam or water; these oxides or acids act as carriers of oxygen from the excess of air present to the sulphur dioxide producing sulphuric acid more or less diluted with water. This is the basis of what is known as the chamber process, as it is carried out in large leaden chambers. 2. By the catalytic or surface action of certain substances, such as platinum, oxide of iron, &c., which under certain conditions have the power of causing the rapid combination of sulphur dioxide and oxygen to form sulphur trioxide. This is the basis of the contact process, and all fuming acid is now made by this method, and also a considerable amount of highly concentrated non-fuming or ordinary sulphuric acid.

It seems probable that a combination of the contact process with the ordinary lead chamber or tower systems would prove advantageous (Wilke, J. Ind. Eng. Chem. 4, 840).

THE LEAD CHAMBER PROCESS.

Early history.—It has long been known that when brimstone and a small quantity of saltpetre are burnt together in moist air or in vessels containing water to absorb the fumes produced, an acid liquid results, which can be concentrated by evaporation. About 1740, Ward started a small factory at Richmond, Surrey, for the preparation of sulphuric acid by such a process. 8 parts of sulphur and 1 part of saltpetre were burnt together in a glass vessel shaped like a bell containing a little water at the bottom and kept warm on a sand-bath. As soon as the fumes from one charge were condensed, a second was introduced and fired, and this was continued until the acid was strong enough for use either at once or after concentration in glass retorts. The first improvement was the substitution by Roebuck in 1746 of lead vessels or chambers for glass bells;

and 50 or 60 years later the use of steam from a separate boiler and of a continuous current of air with a sulphur burner separate from the leaden chamber were introduced. About 1818 a Mr. Hill of Deptford was the first to substitute pyrites for brimstone; in 1827 the Gay-Lussac tower for the recovery of the nitrous fumes carried away in the spent gas was invented, and in 1859 Glover built his first tower for denitrating the nitrous vitriol obtained from the Gay-Lussac tower, and for economising fuel by utilising the heat evolved in the combustion of the pyrites for concentrating the dilute chamber acid and supplying the chamber with a portion of the steam required for the process.

The essential characteristic of the chamber process is the action of the oxides of nitrogen in the presence of water in conveying oxygen to the sulphur dioxide, being reformed each time so that they react over and over again with successive quantities of sulphur dioxide, until the oxidation is practically complete; then the greater part of them may be recovered by absorption from the exit gas and introduced into the process again.

RAW MATERIALS FOR SULPHURIC ACID MANUFACTURE.

Brimstone. Commercial brimstone as used in the manufacture of sulphuric acid contains generally 95–98 p.c. sulphur, 2–5 p.c. ash, which is chiefly sand and calcium sulphate, and also a little bituminous matter. For European consumption the great bulk of it comes from Sicily.

A certain amount of sulphur recovered from alkali waste by the Chance-Claus process, and also from spent oxide of gas works, is used for acid making. The latter is usually dark-coloured owing to the presence of tarry matters. In the United States all the sulphur required for home consumption is obtained from Louisiana and Texas by the Frasch method of extraction (*v. SULPHUR*).

Technical analysis.—Determination of moisture. 100 grms. are roughly crushed and dried at 212° F. in the steam oven until the weight is constant.

Determination of ash.—10 grms. are burnt in a tared porcelain dish and the residue weighed.

Direct estimation of sulphur (Macagno, Chem. News, 43, 192).—50 grms. of finely-ground brimstone are dissolved in 200 c.c. carbon disulphide in a well-stoppered bottle, and the specific gravity of the solution is determined at a given temperature t° . This is reduced to the sp.gr. at 15° by means of the formula

$$S = s \times 0.00014(t - 15)$$

(valid up to 25°), and the percentage of sulphur determined from the following table (p. 564).

F. B. Carpenter (J. Soc. Chem. Ind. 1902, 832) states that if much gypsum is present, it interferes with the carbon disulphide treatment, and must previously be removed by boiling with hydrochloric acid.

Pyrites. Pure iron pyrites has the composition FeS_2 , but commercial pyrites mostly contains more or less copper pyrites $\text{Cu}_2\text{S} \cdot \text{Fe}_2\text{S}_3$, together with varying amount of silicious gangue and small quantities or traces of arsenic, zinc, lead, antimony, selenium, mercury, thallium, &c.

Its value is dependent quite as much on the quantity of copper present as on the amount of sulphur. The analyses given on p. 565 show the composition of the various kinds of pyrites that are, or have been, somewhat extensively used for the manufacture of sulphuric acid. It will be seen from the table that the sulphur may vary from 30 to about 50 p.c. The poorer ores, such as Wicklow containing only from 30 to 35 p.c. sulphur, are seldom used now, manufacturers preferring the richer Spanish and Norwegian ores, owing to the fact that the cost of handling and working pyrites is much the same, no matter what the percentage of sulphur may be, and at the same time the proportion of unburnt sulphur left in the 'cinders' will be the greater the lower the percentage in the ore before burning.

A discussion on the proportional value of rich and poor pyrites has been carried on by

S	Percentage of sulphur	S	Percentage of sulphur
1.271	4×0	1.321	4×12.1
1.274	4×0.6	1.324	4×12.8
1.276	4×1.2	1.327	4×13.5
1.279	4×1.9	1.330	4×14.2
1.282	4×2.6	1.333	4×15.0
1.285	4×3.4	1.336	4×15.6
1.288	4×4.1	1.339	4×16.4
1.291	4×4.8	1.342	4×17.1
1.294	4×5.6	1.345	4×17.9
1.297	4×6.3	1.348	4×18.6
1.300	4×7.0	1.351	4×19.3
1.303	4×7.8	1.354	4×20.1
1.306	4×8.5	1.357	4×21.0
1.309	4×9.2	1.360	4×21.8
1.312	4×9.9	1.363	4×22.7
1.315	4×10.6	1.366	4×23.6
1.318	4×11.3	1.369	4×24.8

Keppelar, Nemes and Uhlman (Chem. Zeit. 37, 1219; 38, 2; 38, 59). It is usual to distinguish between 'free burning' ores and those which possess properties more or less disadvantageous to easy burning. Some varieties decrepitate with explosive violence in the kilns, thereby causing much dust and preventing the access of sufficient air to insure good results (Gyzander, J. Ind. Eng. Chem. 1917, 776). A useful comparative test of this property of ores consists in introducing a few pounds into a cast-iron pot heated to a dull redness in a charcoal furnace or preferably by a large high-power gas burner. After the introduction of the sample the lid is replaced immediately and after the pot has cooled the quantity of ore passing a half-inch mesh sieve is taken as an index of the explosive property of the ore.

A certain quantity of pyrites is obtained in coal mining, and is picked from the coal (coal brasses). It always contains some adhering carbonaceous matter, which causes trouble in the chambers when it is burnt for sulphuric acid making.

Results obtained in the commercial operation of the Gaillard process for the manufacture of sulphuric acid are given by Breton (Chimie et Industrie, 1924, 11, 662). With certain modifi-

cations the process can be applied to gases very poor in sulphur dioxide, such as flue gases from the combustion of fuels high in sulphur.

The dark coloured acid thus produced may be decolorised to a large extent by the addition of a small quantity of potassium chlorate.

Along the coast of the isle of Sheppey in Kent a considerable amount of pyrites has from time to time been collected on the beaches (having been washed out of the clay) and burnt for the production of sulphuric acid.

Analysis of pyrites.—Determination of sulphur (Lunge's Technical Chemists' Handbook, 110). 0.5 gm. pyrites is heated with about 10 c.c. of a mixture of 3 volumes nitric acid (sp. gr. 1.4), and 1 of strong hydrochloric acid, solution being accelerated by heating now and then, and the whole is evaporated to dryness, heated with 5 c.c. more hydrochloric acid and evaporated again. The residue is moistened with 1 c.c. hydrochloric acid, and taken up with 100 c.c. hot water filtered and washed. The insoluble residue consisting of silica and silicates and perhaps some sulphates of lead or barium is usually ignited and weighed. The filtrate is heated with ammonia in slight excess, and the precipitated ferric hydroxide is filtered off and washed three times. The precipitate is then transferred to a beaker and redissolved in the smallest possible quantity of hydrochloric acid, again rendered alkaline and the reprecipitated hydroxide washed until free from sulphates. If the filtrate and washings exceed 200 c.c. they are concentrated, slightly acidified with hydrochloric acid, heated to boiling, and 20 c.c. of a 10 p.c. solution of barium chloride (also hot) added. The boiling should be continued for five minutes. The precipitate is allowed to stand half an hour, the clear portion run off through a filter, and the residue heated with 100 c.c. of boiling water and allowed to settle 2 or 3 mins. This is again poured through the filter, and the washing by decantation repeated three or four times. The precipitate is finally transferred to the filter, washed, dried, and ignited, and the sulphur calculated from the weight of barium sulphate obtained. If the iron is not first removed a deficiency of 1-2 p.c. is apt to be occasioned owing to the solubility of barium sulphate in solutions of iron salts; whilst, on the other hand, a small quantity of ferric oxide is present in the ignited precipitate due to the precipitation of a double sulphate of iron and barium (Pattinson, J. Soc. Chem. Ind. 1905, 10; Jannasch and Richards, J. pr. Chem. [ii.] 39, 321; J. Soc. Chem. Ind. 1889, 819). Lunge (Zeitsch. angew. Chem. 1889, 473; J. Soc. Chem. Ind. 1889, 966) finds that the precipitated ferric hydroxide may carry down some basic iron sulphate if the liquid is boiled until the smell of ammonia is all but gone, but not if the method is carried out as above described. A large number of other methods may be employed for the estimation of sulphur in pyrites, among which may be mentioned that of Fresenius (Zeitsch. anal. Chem. 1877, 335), in which the pyrites is fused with a mixture of sodium carbonate and potassium nitrate. That of List (Zeitsch. angew. Chem. 1903, 414), in which sodium peroxide is used, and Zulkowsky's method in which the pyrites is burnt in a stream of oxygen and the vapours are absorbed by potassium hypobromite solution.

	Spanish and Portuguese			Norwegian		Irish (Wicklow)	Welsh	Belgian	Cornish	West- phalian	French	
	Tharsis	Rio Tinto	San Domingo	First quality	Second quality						Mène	Scheurer- Kestner
	Highly cupriferous		'Masons'									
Analyst . . . {	Pattinson	—	Claudet	McCulloch	McCulloch	Pattinson	—	McCulloch	Clapham	Pattinson		
Sulphur . . .	49·30	49·44	49·00	46·15	38·17	44·20	30·60	45·60	24·0 to 34·9	45·60	45·2 to 47·6	45 to 48
Iron . . .	41·41	42·56	43·55	44·20	32·80	40·52	30·69	38·52	27·1 ,, 69·7	38·52	39·0 ,, 39·7	—
Copper . . .	5·81	3·36	3·20	1·20	1·10	0·90	0·01	nil	0·4 ,, 4·6	—	—	1 to 2
Lead . . .	0·66	0·51	0·93	—	—	1·50	0·07	—	0 ,, 7·4	0·64	—	—
Zinc . . .	trace	0·80	0·35	2·10	2·32	3·51	0·09	6·00	0 9·0	6·00	—	—
Arsenic . . .	0·31	0·38	0·47	nil	trace	0·33	0·03	trace	0 ,, 1·2	tarce	present	—
Lime . . .	0·14	—	0·10	2·55*	11·90*	0·24	3·98	0·11*	0 ,, 3·6*	0·11	—	—
Silica and insoluble matter . . .	2·00	0·58	0·63	3·20	12·20	8·80	21·68	9·00	2 ,, 38·7	8·70	9·6 to 11·0	—
Alumina, magnesia, oxygen, moisture, and matters not es- pecially determined	0·37	2·48	1·77	0·60	1·51	0·34	12·85	0·77	—	0·73	3 9 ,, 4·8	—
	100·00	100·11	100·00	100·00	100·00	100·34	100·00	100·00	—	100·30	—	

* Calcium carbonate.

To determine the sulphur left in the burnt ore, the material is dissolved in *aqua regia* and evaporated, the residue taken up with hydrochloric acid and water and precipitated as above by barium chloride whilst boiling, the removal of iron by ammonia being omitted.

J. Watson (J. Soc. Chem. Ind. 1888, 305) heats 3.2 grms. of the burnt ore with 2 grms. of sodium bicarbonate in a nickel crucible over a low Bunsen flame for 5 or 10 mins.; the mass is then cautiously stirred with a wire stirrer, and the heat increased for 10–15 mins. more when the oxidation of the sulphur is complete. Finally, the mass is treated with water, and the excess of alkali titrated with standard acid, using methyl orange as indicator.

Lunge has investigated this method (Zeitsch. angew. Chem. 1889, 239; J. Soc. Chem. Ind. 1889, 572–1890, 1014), and finds that it is not only the simplest and cheapest, but also the quickest and most accurate test for the purpose.

Determination of arsenic.—The method recommended in Lunge's Technical Chemists' Handbook is that of Reich, as modified by McCay. 0.5 gm. is decomposed by concentrated nitric acid, the solution evaporated nearly to dryness, and fused with 4 grms. Na_2CO_3 and 4 grms. KNO_3 for 10 mins. The mass is extracted with hot water, filtered, the filtrate made just acid with nitric acid, and the arsenate precipitated with silver nitrate solution, the excess of acid being carefully neutralised with calcium carbonate. The silver arsenate is dissolved in nitric acid, and the silver estimated by titration with ammonium thiocyanate, or the solution may be evaporated to dryness and the silver arsenate weighed. A list of other methods and modifications will be found in Lunge, vol. i. Supplement, 1917.

Other metallic sulphides have recently come into considerable use for the manufacture of sulphuric acid, chiefly owing to legislation which has forced zinc and copper smelters to take measures to deal with the sulphurous gases liberated from their furnaces.

Zinc blende, which is the principal zinc ore, contains between 20 and 30 p.c. of sulphur, and the sulphur dioxide formed during the preliminary roasting process is very largely utilised for the production of sulphuric acid.

The following analyses of Rhenish blende are given by Minor (Chem. Zeit. 1889, 1602)—

Sulphur .	30.24p.c.	27.94p.c.	22.11p.c.	21.05p.c.
Zinc .	27.76	31.92	40.29	37.81
Iron .	15.98	13.12	2.06	2.33
Gangue .	21.02	27.02	35.54	38.84

The products from the roasting of copper ores and copper matte are now also largely used for vitriol manufacture.

The use of the **spent oxide** of gas-works for vitriol making has increased considerably during the last few years owing to its increased production. The sulphuretted hydrogen in coal gas is removed from it by means of a mixture of hydrated ferric oxide and sawdust, which can be made to take up so much sulphur by alternately exposing it to coal gas and air, that a product is obtained containing as much as 60 p.c. of sulphur available for conversion into sulphuric acid.

COMPOSITION OF SPENT OXIDE.

(Davis, Chem. News, 36, 189.)

	From precipitated $\text{Fe}(\text{OH})_3$	From bog- iron ore
Ferric hydroxide	17.74–19.36	15.96–26.42
Sawdust	1.98–4.72	1.14–3.72
Calcium carbonate . .	0–1.04	0–1.73
Ammonium thiocyanate	1.99–2.74	0.94–1.93
„ ferrocyanide	trace	trace–0.21
Tarry matters . . .	0.72–1.22	0.92–1.14
Sulphur	62.44–67.18	48.76–57.44
Insoluble in dilute HCl	3.66–5.47	9.74–11.42
Prussian blue . . .		trace–0.17
Moisture (by difference)	4.72–5.76	7.22–10.82

Davis (Chem. News, 29, 30; 36, 189) gives a number of other analyses.

The available sulphur in spent oxide is usually estimated by extracting the free sulphur in a Soxhlet extraction apparatus by means of carbon disulphide and weighing it; but this method is not altogether satisfactory as the tarry matters are dissolved out also by the disulphide, whilst any sulphur existing in the insoluble form is not estimated. A more satisfactory method is to burn the spent oxide in a current of oxygen, and to absorb the evolved sulphur dioxide in bromine water, estimating the sulphuric acid formed by precipitation with barium chloride. The method described by Dennstedt and Hasslar (Zeitsch. angew. Chem. 1905 and 1906) is very satisfactory. Quartz is preferable to the platinised asbestos. Davis and Foucar (J. Soc. Chem. Ind. 1912, 100) convert the sulphur into sodium thiocyanate by digestion with alcoholic sodium cyanide solution, the thiocyanate being then titrated with *N*/20 silver nitrate solution in the usual way.

Sulphuretted hydrogen, recovered from alkali waste, and from ammonia liquor during the manufacture of sulphate of ammonia is sometimes used for the manufacture of sulphuric acid. It is burnt either by itself or in conjunction with spent oxide.

Nitrate of soda. In the early days of vitriol-making, *saltpetre*—i.e. potassium nitrate—was the only salt practically available; but this has so long been superseded by the cheaper 'Chile saltpetre' or 'soda nitre' (approximately pure sodium nitrate¹) that the term *nitre* in the vitriol trade is always understood as referring to the latter.

PLANT USED FOR THE MANUFACTURE OF SULPHURIC ACID BY THE CHAMBER PROCESS.

In a modern sulphuric acid plant for the manufacture of chamber acid there are required: (1) A burner for the production of the mixture of sulphur dioxide, oxygen, and nitrogen; (2) an arrangement for introducing nitrogen oxides or nitric acid into the burner gas; (3) a steam generator; (4) one or more large leaden chambers in

¹ The average composition of sodium nitrate as used for vitriol making may be taken to be:

Sodium chloride . . .	0.5
Sodium sulphate . . .	0.75
Moisture	2.75
Total 'refraction' (impurities) . . .	4.00
Sodium nitrate (by difference) . . .	96.00
	100.00

When the chloride present exceeds 1 p.c., the substance is apt to cause a considerable amount of loss of nitrogen oxides in the chambers.

which the oxidation can take place; (5) a Gay-Lussac tower for recovering the bulk of the nitrogen oxides from the exit gases; and (6) a Glover tower for introducing these oxides again and concentrating the chamber acid.

The production of sulphur dioxide. Brimstone burners.—The simplest form consists of a brick chamber covered by an arch, the bottom being formed by an iron plate. There is a door in front, through which the brimstone is charged from time to time, and at the back a pipe for taking

away the gas. The burner is started by heating the iron plate by lighting a small fire on it, and when hot enough to ignite the sulphur, the latter is charged at regular intervals through the door, which slides in a frame and is adjusted by a chain and balance weight, the admission of the necessary amount of air being regulated by it. There is an air channel beneath the iron plate to prevent it from becoming too hot, and so causing the sulphur to sublime. The nitre pots containing the nitre and sulphuric acid may be

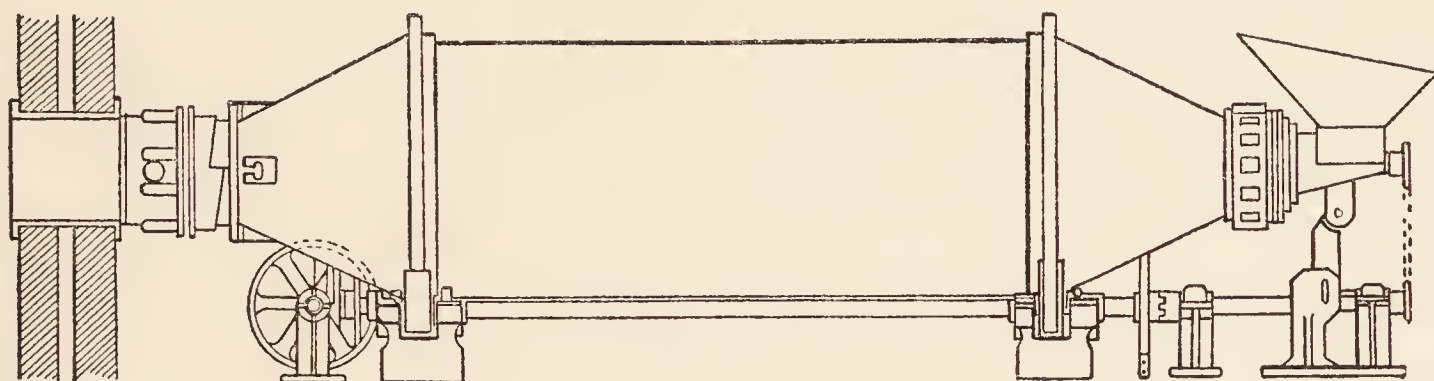


FIG. 2.

placed in the midst of the burning sulphur, or better, in a brick extension at the back of the burner. Several furnaces of this kind are usually combined together and charged at different times in order to obtain a gas of as uniform composition as possible. Each of them with plates 8 ft. by 4 ft. can burn 5 cwts. of brimstone in 24 hours. In some cases the gas passes from the burner into an upper chamber divided into two compartments, so that it has to pass from back to front and then back again before passing to a common flue; some additional air is admitted into this upper chamber in order to burn any sulphur which sublimates.

Harrison Blair's continuous burner consists of three parts. In front is a brick chamber into which the brimstone is charged either continuously by means of a hopper or at regular intervals. Here just sufficient air is admitted to keep up the heat of the furnace. The sulphur partly sublimates into a second compartment at the back, where sufficient air is admitted to complete the combustion, and the gas then passes to a chamber above in which the nitre pots are placed.

Glover's brimstone burner, in addition to the burner plate and feeding hopper, was provided with a chamber containing a chequer work of firebrick in the upper portion, serving to promote the complete combustion of the sulphur. Miles and Sarginson (*J. Soc. Chem. Ind.* 1922, 183 T) describe a similar type which was used to a considerable extent during the war. See also Prentice, *Eng. Pat.* 197845, 1922; Clayton, *Eng. Pats.* 141661 and 161439, 1920; Ellis, *U.S. Pat.* 1289417. Patterson and Cheney (*J. Ind. Eng. Chem.* 4, 733) give a description of plant for the manufacture of sulphuric acid from sulphur. The rotary burner of Tromblee and Paull shown in Fig. 2 (*U.S. Pat.* 749311, 1904) is now largely used. The cylindrical iron shell of the burner is supplied with roughly crushed sulphur by worm-gear at the lower part of the hopper. The molten sulphur forms an unbroken coating on the inside lining of the furnace, which is caused to rotate slowly. A small chamber is provided, at the exit end, to

ensure the complete combustion of any sulphur which may be carried forward from the body of the furnace. The composition of the gas is readily controlled and the maintenance charges are small. From $2\frac{1}{2}$ to $2\frac{3}{4}$ tons of sulphur can be burned in a day. A vertical stationary type containing a series of trays is also used. Fig. 3

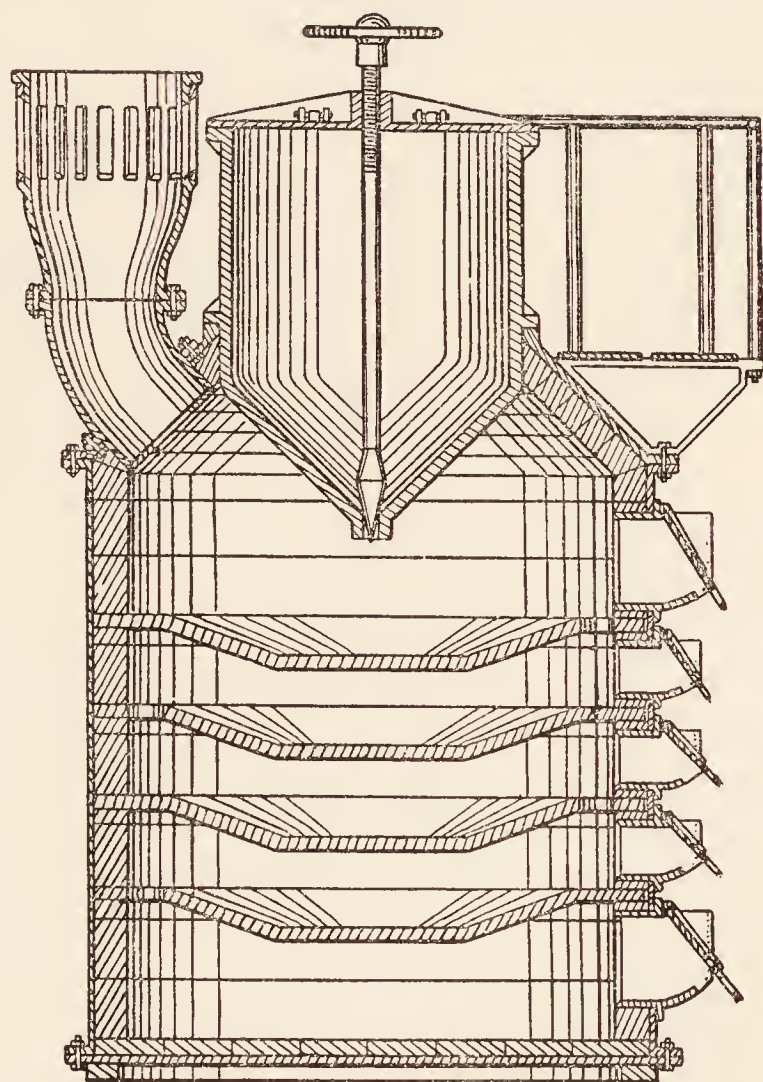


FIG. 3.

represents that of Hinzke (*U.S. Pat.* 1149765, 1915). The burner consists of a casing lined with brickwork which supports a series of trays. The supply of molten sulphur is regulated by means of a plug at the bottom of the melting pot and is so adjusted that combustion is completed before the last tray is reached. Any

sulphur which has escaped combustion in the main portion of the furnace is burned in the additional chamber which forms part of the outlet pipe. This design is economical in floor space, and the absence of any motive power is an advantage. Burners are made in various sizes, with capacities from 250 lbs. to 12 tons per 24 hours. For small units and where a concentrated gas is essential, burners of the type shown in Fig. 4 are useful. The small type of burner chiefly used for sulphite pulp manufacture should in all cases be provided with a secondary air inlet if sublimation is to be avoided. Large rotary sulphur burners equally require a secondary air inlet and also a combustion chamber. Furnaces of this type for the production of gas commercially free from oxygen have been described (Eng. Pats. 100939, 1916; 11750, 1912; 21996, 1911; and Fr. Pat. 480294).

Pyrites burners.—The bulk of the pyrites used for sulphuric acid manufacture arrives in large fragments which have to be broken either

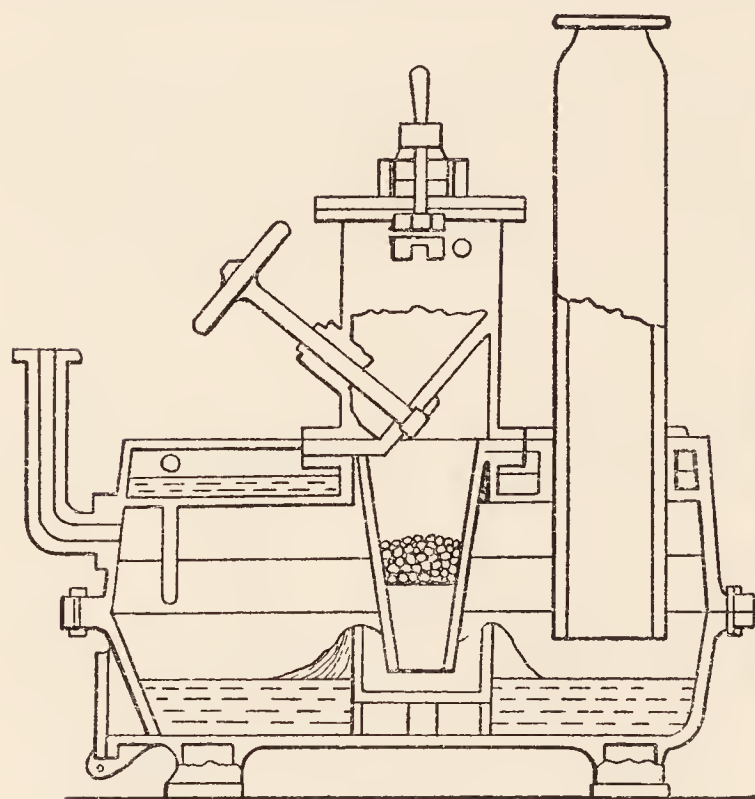


FIG. 4.

by hand or by crushing machines to a size suitable for burning. The broken ore is divided into 'smalls' and 'lumps' by screening through a $\frac{1}{4}$ -in. or $\frac{1}{2}$ -in. sieve. The lumps should all pass through a screen with about 3-in. holes. Crushing machines produce more smalls than breaking by hand; but in view of the fact that pyrites smalls are now almost exclusively burnt in mechanical furnaces, this production of smalls is no detriment, and hand breaking is becoming obsolete.

Burners for lump ore.—These are generally known as kilns and they are constructed in such a way that the heat of combustion of the ore is utilised for maintaining the process without any extraneous fuel.

They are built in two rows back to back to avoid loss of heat. The walls are of fire-brick, the fronts being encased by cast-iron plates provided with various doors necessary for working. They are rectangular in section, and the ore in each kiln rests on a grate consisting of movable bars of 2-in. square section which can be rotated by a key which will fit

on to the ends projecting through the front plate. By this means the space between the bars may be varied, being 2 ins. when their sides are vertical, and only $1\frac{1}{4}$ ins. when they are on edge. By rotating these bars the burnt ore is worked down into the ash pit below. The front of each kiln is also provided with a charging door about 2 ft. above the grate, or 14 ins. in more recent designs, and an ash-pit door below the bars for removing the burnt ore. There is usually another opening between the charging door and the bars, which is only used occasionally when the ore forms slags or clinkers, which have to be raised and removed through the charging doors. The projecting ends of the bars are also boxed in and doors provided. The air admitted to each kiln is regulated by openings in the ash-pit doors. A structural objection to this design is the excessive outward thrust to which the front of the burners is subjected. In more recent types the upper arch is cross sectional, and the lower arch at right-angles to the front of the kilns (see Fig. 5). In some cases, usually in Continental works, the side walls do not completely separate the kilns, and the gases mix in the space above the burning ore, so that a common flue on the top of each row is not required. The ore may also be charged through the top by means of a hopper closed by a cone which can be lowered by a lever worked from the front of the kiln, and if the latter is well raised above the ground level the bottom of the ash pit may also be in the form of a hopper closed by a sliding door, so that the burnt ore can be dropped into a receptacle below the burner; or the ash pit may be made deep enough to allow the introduction of an iron bogie into which the burnt ore drops, and it can be thus expeditiously removed. The walls generally have a slight slope inwards below the charging door, so that the area at the grate bar level is a little smaller than that at the charging door. English burners are usually 4–5 ft. wide, and $4\frac{1}{2}$ –6 ft. from back to front at the grates. The depth of ore, which is determined by the height of the working door above the bars, may vary from 14 ins. to 2 ft. 6 ins., and depends usually on the percentage of sulphur in the pyrites, poor ores requiring a much greater depth than rich ores. In England for rich ores a depth of 2 ft. is employed in some works, but 16–18 ins. or even 12–14 ins. is quite usual both on the Continent and in England.

In order to start a burner it is filled up with burnt ore up to about 3 ins. below the working door, and the top layer is brought to a dull-red heat by lighting a coke fire on the top. After about 24 hours the ore is hot enough, when the partially burnt coke is removed as far as possible, and the charge of pyrites is thrown in by the kiln-man and spread evenly over the surface. The amount charged will depend on the area of the kiln, the richness of the ore and the length of time between two successive charges. Usually with large kilns of 25–30 square ft. area the charge is put on every 24 hours, and with rich Spanish ore containing 48 p.c. sulphur, 6–9 cwts. is the weight charged, or from 30–40 lbs. per sq. ft. area. With poorer ores, such as Westphalian, containing 40–42 p.c. sulphur, 50–60 lbs. may be burnt per 24 hours per sq. ft. area (Hasenclever). Davis (Chem. Engineering, ii. 88) states that with Aguas

Tenidas ore containing 50 p.c. sulphur he has burnt 55 lbs per sq. ft. per 24 hours down to 1 p.c. sulphur, but the area employed only amounted to 14 sq. ft. With kilns of small area it is more usual to charge every 12 hours.

When the charge appears to be burnt off and shows no more sulphur flames (18–20 hours after charging for 24-hour charges) the surface is broken up by poking and raking, a certain amount of burnt ore being at the same time allowed to drop into the ash pit by turning the grate bars, and the burner gradually cools and is ready to be charged again at the end of the 24 hours. The amount of air necessary is regulated by opening or closing the slides or holes in the ash-pit door as required. Usually 20–24 kilns are charged in rotation during the 24 hours, in order that the composition of the burner gas may be as uniform as possible. By the time the ore reaches the bars (5 or 6 days after it is charged) it should be nearly cold, and should not contain more than 3 p.c. sulphur, in the case of rich cupreous ores such as Rio Tinto or Tharsis pyrites. With non-cupreous pyrites the sulphur may be burnt as low as 1 p.c. The regulation of the draught requires considerable care. If too

little is employed the ore will form slags or clinkers owing to the formation of fusible iron monosulphide FeS , and at the same time sulphur will sublime. These slags must not be allowed to get down on the bars, where they would stop the draught, but must be lifted by means of heavy pokers and broken up and pulled out of the working door. If the draught is too great the burners get cold and will not light readily when charged, and the burner gas will get too weak owing to the excess of air employed.

The air supply for a set of kilns is controlled behind the burners by means of a damper which may be placed either before or behind the chambers, and before each burner by holes in the ash-pit door. If the Glover tower and chambers are well raised above the kilns, or mechanical draught is employed, these means of control may be so regulated that no escape of gas takes place when the working doors are open for charging or poking, but at the same time a good deal of air enters and disturbs the uniform working of the chamber process; and this also happens when the ash-pit door is open during the removal of the burnt ore. Charging by means of a hopper in the top of the kiln, and

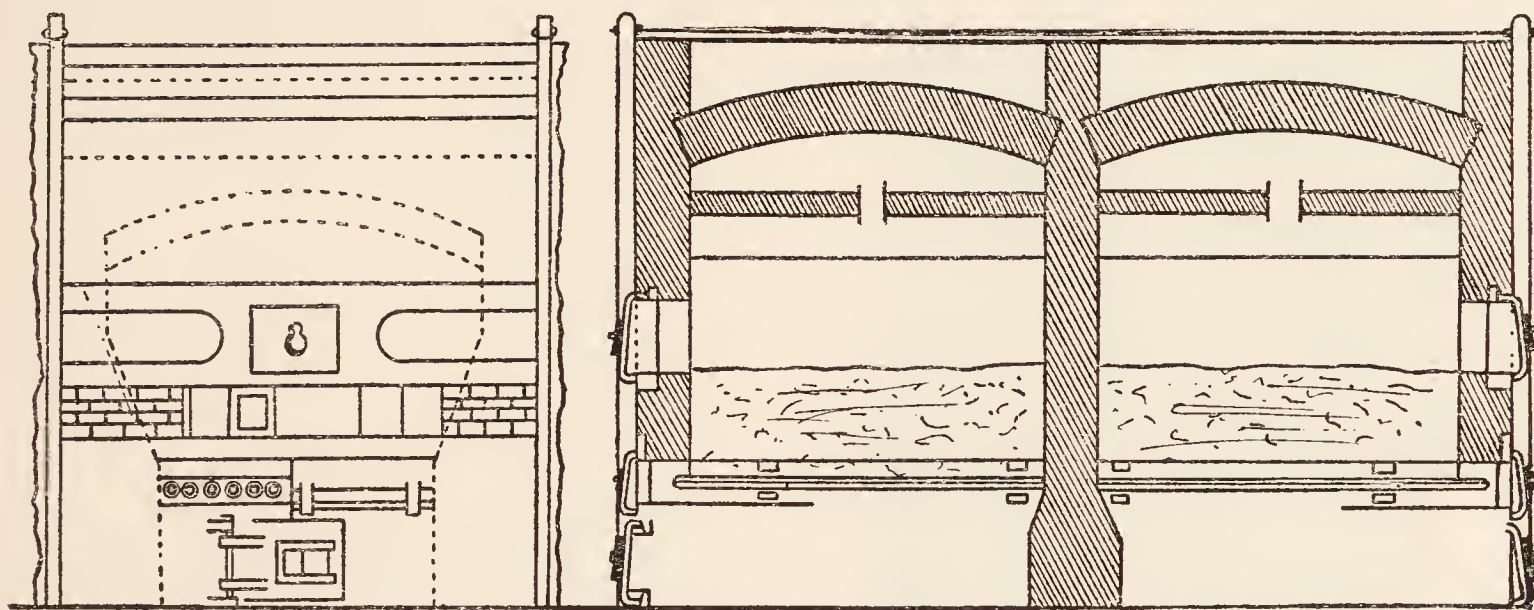


FIG. 5.

discharging the burnt ore in a similar way below the ash pit, reduces this disturbance to a minimum. In many cases every time a working door is opened a good deal of gas escapes into the atmosphere; attempts have been made to prevent this by closing all the air slides in the ash-pit doors whenever a kiln is being charged (Norrington, Eng. Pat. 4131, 1878); or by connecting the ash pit when a door is open by means of a special flue with a chimney, the draught from which is so regulated that no burner gas is drawn down into it, but it is sufficient to prevent any blow out at the door during charging. The admission of air may also be checked from time to time by analyses made of the percentage of sulphur dioxide in the burner gas and of oxygen in the gases escaping from the chambers, the latter figure giving the average amount of surplus air admitted during the whole process of charging, burning, poking, &c.

Koppers (D. R. P. 288322, 1913) burns pyrites in a kiln provided with a revolving conical grate into which air is introduced, which passes by fine openings into the kiln.

(Mlle.) G. Marchal (Bull. Soc. chim. 1924,

[iv.] 35, 43) has made a study of the dissociation of iron pyrites (into ferrous sulphide and sulphur) in a vacuum and in an atmosphere of nitrogen. In a vacuum, dissociation begins at 500° , is much more rapid at 550° , and, at 670° – 680° , is complete in 8 hours, large pieces of pyrites undergoing disintegration during the progress. At 700° – 800° the sulphur condenses in a well-defined form, and possibly could so be extracted from pyrites on the large scale. At 850° dissociation is complete in two hours. At higher temperatures (1200°) the residue is a mixture of ferrous sulphide and a small amount of iron.

In an atmosphere of nitrogen dissociation is very rapid at 850° (Chem. Soc. Abstr. 1924, 126, ii. 187).

Thompson and Tilling (J. Soc. Chem. Ind. 1924, 43, 37 T) have collected the data, and in some cases re-determined the conditions of the desulphurisation of iron pyrites. A constant volume of gas was passed over a known weight of pyrites heated to a known temperature, and the percentage of sulphur (soluble and total) in the residue ascertained after treatment. Graphs are given expressing the results obtained when

using air, steam, carbon dioxide, carbon monoxide, hydrogen, and coal gas.

The vapour pressures of sulphur dioxide, sulphur trioxide and oxygen during the oxidation of pyrites was also measured. The vapour pressures of these gases over heated ferric sulphate, the basic sulphate $\text{Fe}_2\text{O}_3 \cdot 2\text{SO}_3$ and ferrous sulphate have been investigated by Bodenstein, Pohl and Suzuki (Zeitsch. Elektrochem. 1905, 11, 373; 1910, 16, 912); Keppeler and D'Ans (Zeitsch. physikal. Chem. 1908, 62, 89); also Wöhler, Plüddemann and Grünzweig (Ber. 1908, 41, 703; 1913, 43 1587). Allen and Lombard (Amer. J. Sci. 1917, 43, 175) examined the dissociation pressure of FeS_2 .

Burners for smalls.—At one time the use of smalls burners was mainly confined to the working up of the dust of the pyrites produced in transport or during breaking; if this does not amount to more than $7\frac{1}{2}$ p.c. of the ore it may be burnt with the lumps if it be carefully distributed along the sides and back, and in the front corners of the kilns, leaving the central part free; or

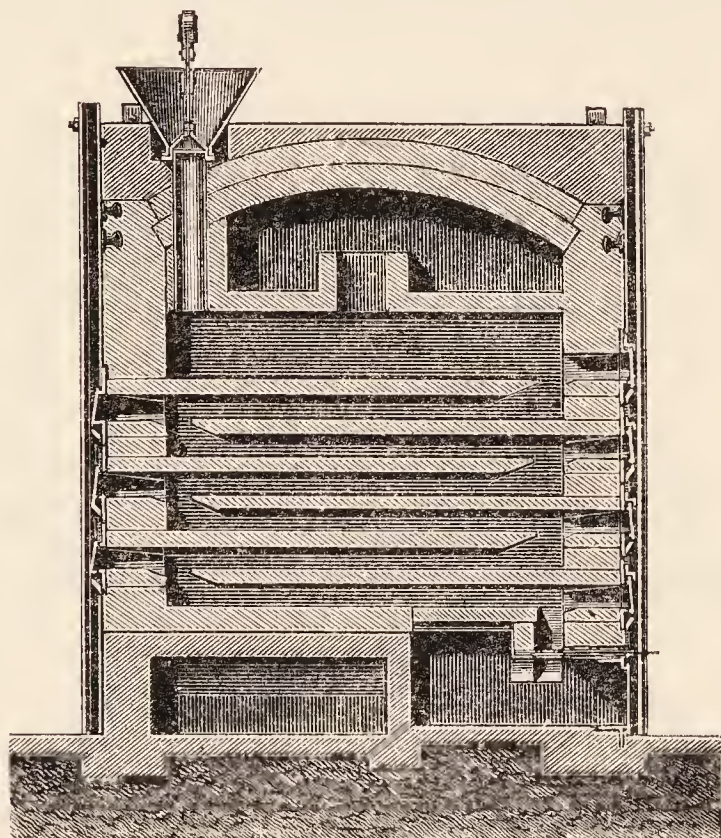


FIG. 6.

it may be made into balls or cakes after grinding up with water and drying on the top of the kilns; incipient oxidation takes place, and the mass binds together sufficiently hard to burn with the lumps. Formerly balls were made by the addition of clay and drying, but this method is no longer used, as the clay interfered with the burning and with the subsequent extraction of copper. During recent years large quantities of smalls have been received direct from the mines, being produced during the mining operations or from ore from which the copper has been extracted by weathering and washing out with water. Special smalls burners are necessary for burning these. In the earliest type, of which Spence's is an example, the ore was heated in a closed muffle or roaster by the flame from a coal fire, but this has long been superseded by arrangements requiring no extraneous heat. Sometimes the smalls are burnt on fire-clay shelves arranged above the burning pyrites in ordinary lump ore kilns, but this method has not proved satisfactory, much surplus air

entering the burner during charging and removing the dust. Hasenclever and Helbig employed a series of alternate sloping shelves, one above the other in a square tower up which ordinary kiln gases passed, but this type of burner has become obsolete. In the Maletra furnace the heat of combustion of the smalls alone is sufficient to desulphurise the ore, and this type of burner has been worked successfully for many years both on the Continent and in England. As originally constructed, the burners are arranged back to back, there are six shelves to each, and each shelf is provided with a working door in front. In Schaeffner's modification (Fig. 6) the burners are arranged in a single row, there are seven shelves, the doors being alternately arranged four in front and three at the back. The chief drawbacks to this type of furnace are the considerable amount of labour required in working, and the excessive introduction of 'false' air during the frequent opening of the doors for the purpose of moving the ore from shelf to shelf. The cost of repairs for the furnaces is also considerable.

W. Crowder (J. Soc. Chem. Ind. 1891, 295) gives the following figures as the average of a number of daily tests of the sulphur contained in the partly-burnt ore on each of the seven beds of a Schaeffner kiln, charged with pyrites containing 50 p.c. sulphur every 8 hours, so that it took 56 hours for the ore to pass through the kiln from shelf to shelf:—

No. 1 shelf	.	.	32.27	32.81
" 2 "	.	.	21.41	17.55
" 3 "	.	.	12.77	11.09
" 4 "	.	.	6.39	5.03
" 5 "	.	.	4.08	3.42
" 6 "	.	.	2.35	2.56
" 7 "	.	.	2.27	1.96

Mechanical smalls burners.—The MacDougall furnace, patented in 1868, was the first burner of this type to be employed for burning smalls. It consists of a cast-iron cylinder, 6 ft. diameter by 12 ft. high, made in seven sections, bolted together, and is divided into seven chambers by firebrick arches. Through the centre a vertical cast-iron shaft passes to which are attached a number of rakes, the teeth of which are so arranged that as the shaft revolves they move the ore alternately from centre to periphery and from periphery to centre on successive beds. The ore is continuously charged on to the top of the furnace by an elevator, and after travelling to the outer edge it drops into a receptacle from which it is continuously pushed into the top closed chamber by a ram, the rate of movement of which regulates the feed, and after passing from shelf to shelf is finally discharged at the bottom completely burnt. The air is continuously supplied by means of an air pump into the lowest chamber, and travels up the furnace in the opposite direction to the ore, the burner gas leaving the top section by a pipe leading to the chambers. The enormous amount of dust carried forward was the chief drawback to the MacDougall furnace when first introduced, and also the great wear and tear of the shaft and rakes due to excessive heat. The first-mentioned drawback was due to the small diameter of the burner, and the method of introduction of the air. The wear and tear was considerably

reduced by making the shafts and rakes hollow and cooling them by air, and the dust carried away was somewhat reduced by substituting ordinary induced draught for the air pump, and providing dust chambers with perforated baffle plates for the interception of the dust (MacDougall, Eng. Pat. 3985, 1883). The MacDougall furnace has been further improved by Frasc (Zeitsch. angew. Chem. 1894, 15), who employs water as the cooling medium for the shaft and rakes. Another modification is the Herreshoff burner (Fig. 7), in which the shaft is air-cooled. It is described by Gilchrist (J. Soc. Chem. Ind. 1899, 460); Hartmann and Benker (Zeitsch. angew. Chem. 1906, 1125 *et seq.*). It consists of an upright steel shell lined with firebrick about 10 ft. high and 10 ft. diameter; the arms or rakes are inserted into sockets in the shaft and can be detached and

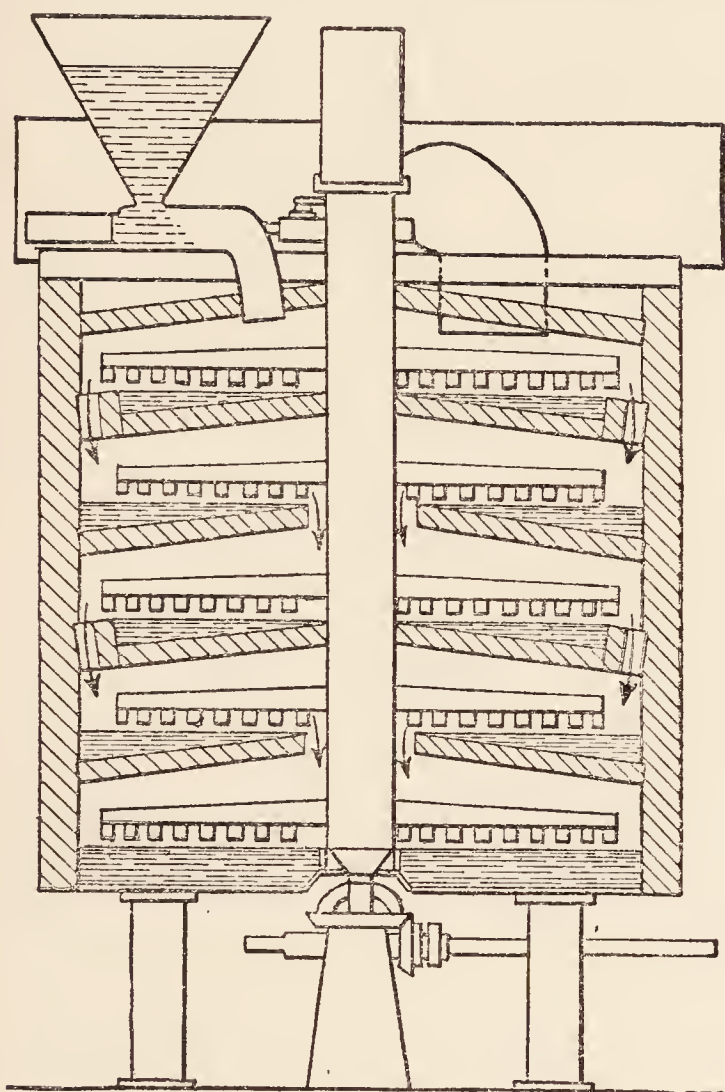


FIG. 7.

replaced in a few minutes. There are five shelves with two rakes to each shelf. The ore is fed automatically from a hopper on to the top shelf by means of a plunger moving backwards and forwards, so much dropping at each revolution of the shaft. These furnaces will burn up to 3 tons of rich Spanish pyrites per 24 hours, between 2 and 3 p.c. of sulphur being left in the 'cinders,' and will furnish a richer gas than hand-worked furnaces. The hot air leaving the hollow shaft may be utilised for drying the ore by a suitable arrangement. The power required is about $\frac{2}{3}$ h.p. per furnace.

Spence's mechanical furnace, patented in 1878, has met with some success in America (Lunge). It is a shelf burner of the Maletra type, provided with mechanical stirrers which travel to and fro from the front to the back of each shelf.

In the Kaufmann furnace, which is of the Herreshoff type, there are only three shelves, and the teeth on the rakes are so constructed that the ore is moved forward a certain distance, and then back a shorter distance during each revolution (Truchot, Proc. Seventh Int. Congr. App. Chem. 1909; J. Soc. Chem. Ind. 1911, 280). The O'Brien furnace (U.S. Pat. 775147, 1904) is also a modification of the same type. The Wedge furnace represents the latest development of the mechanical burner. It can be constructed to burn 40 tons of pyrites per 24 hours, and is six or seven times as large as the ordinary Herreshoff burner. The shaft consists of a hollow steel cylinder, 4 ft. diameter, and its main feature is that it permits of repairs being made without interruption of its working. The arms are water-cooled (Hasenclever, J. Soc. Chem. Ind. 1911, 1291). Other furnaces of this class are those of Ramen and Thorba.

The new Herreshoff furnace (U.S. Pat. 976175, 1910) is also constructed to burn up to 20 tons pyrites per 24 hours. Both shaft and arms, which are hollow and of cast-iron, are cooled by forcing air through them by means of a fan. Part of the hot air so obtained is utilised for the combustion of the ore by introducing it into the lower beds, considerably increasing thereby the capacity of the furnace (Gilchrist, J. Soc. Chem. Ind. 1899, 459).

The chief advantage of the mechanical burner over hand-worked kilns is the saving of labour, but a good deal of this is counterbalanced by the cost of repairs. Lütty states (Zeitsch. angew. Chem. 1905, 1253) that hand-worked burners are cheaper than mechanical burners if the cost of labour is below 4s. per man per shift. An additional advantage is the regular composition of the burner gas obtained, owing to the fact that it is seldom necessary to open the doors of the furnaces.

Wherever smalls burners are employed it is necessary to provide a dust chamber to arrest the bulk of the dust carried forward from the furnaces. This chamber usually consists of a large expansion of the flue with or without baffle walls arranged in various ways, the main objects being to retard the speed of the gaseous current and to offer large surfaces on which the dust can deposit. At the same time the gas must not be too much cooled, nor must the baffle walls interfere seriously with the draught. If the surfaces are arranged in the direction of the current itself they do not seriously affect the draught, and yet collect a large amount of dust. With mechanical burners the amount of dust carried forward is very considerable, and it may contain as much as 10 p.c. unburnt sulphur. O'Brien's dust-catcher, described by Falding (Min. Ind. ix. 623), consists of a hopper-shaped iron shell 8 ft. wide at the top and 12 ft. high, lined with firebrick. The gas enters tangentially at the top and leaves by a central vertical pipe. The separation of the dust is due to centrifugal action, and it drops to the bottom and is discharged. 75 p.c. of the dust from five Herreshoff furnaces is retained by it. Benker and Hartmann (Fr. Pats. 372644, 1906; 387456, 1908) filter the gases and free them from dust by passing them horizontally through vertical filters composed of pieces of firebrick or burnt ore, the filtering material being continuously

removed from the bottom and returned to the top after separating the dust.

Guttmann (J. Soc. Chem. Ind. 1903, 1331) states that good results have been obtained from tangential dust chambers on the principle of Meyer's acid chambers.

The Howard dust-chamber (U.S. Pat. 896111, 1910) consists of a brick chamber containing a large number of horizontal steel plates $2\frac{1}{2}$ inches apart, between which the gases pass from one side to the other and deposit the dust on the large surface so obtained. The removal of dust may also be accomplished by the introduction of a wash tower through which the gases pass before entering the Glover tower. By this means the contamination of the acid by dust is confined to a small percentage of the acid made. The gases for use in the chamber system require to be reheated after passing the wash tower. In the Curtius tower system the gases may be cooled to 250° or even 150° (Eng. Pat. 28550, 1913). The application of high-tension electric discharge to separate both dust and fume from gases is extending. It is likely that the employment of such types of apparatus as those associated with the name of Cottrell will become more general (J. Ind. Eng. Chem. 3, 542; 9, 26; 10, 35; J. Soc. Chem. Ind. 1918, 389 R; Elec. J. 14, 226; Chem. and Met. Eng. 1918, 309; Chim. et Ind. 1921, 5, 143).

Ignoring radiation, the gas from a mechanical burner would leave at a temperature of 850° . This is calculated to be reduced by radiation to 632° . To effect a further reduction to 500° , the most advantageous temperature, it is necessary to circulate through the shaft and arms a quantity of air equal to about half that necessary for combustion, or if the circulating air is used for effecting the combustion, $1\frac{1}{2}$ times the quantity necessary should be circulated. A burner is described in which all the hearths except the lowest operate independently, being fed from the burner top at their outside edges. The two revolving arms in each hearth are so arranged that one draws the pyrites towards the centre and the other pushes it to some extent back again. It is finally drawn to the centre and falls down the shaft to the bottom hearth, on which combustion is completed. The combustion air is drawn from the air which cools the shaft and arms. The design, it is claimed, minimises dust and allows the hearths to be considerably inclined to the horizontal, thus reducing the outward thrust. For the separation of dust Moritz (Chim. et Ind. May, 1924, 364) prefers filters constructed of perforated sheets of metal, a number being placed close together. The burner gases should enter the Glover tower at 250° . The heat removed from these in cooling from 500° is calculated to be more than sufficient to concentrate all the Glover acid to d 1.84. It is proposed to effect this concentration in an inclined channel of volvic lined externally with lead and connected to the dish of the Glover.

Furnaces for zinc blende.—For this purpose, muffle furnaces were first employed, identical in principle with Spence's furnace for pyrites smelts, but not more than 60 p.c. of the sulphur could be utilised for sulphuric acid production from these, and they have been superseded by various forms of shelf-burner, which combine the

heat produced by the burning of the ore with heat applied externally, but in such a manner that the fire gases are kept entirely separate from the roasting gases. Eichorn and Liebig (D. R. P. 21032) were the inventors of this type of furnace, by which the whole of the sulphur could be utilised for vitriol manufacture, and it has been modified and improved by Hasenclever in the Rhenania furnace, which consists of three superposed muffles, around which the fire gases circulate, and the ore is moved from one muffle to the next below, as in the Maletra furnace (Lunge-Cumming, Manufacture of Acids and Alkalis, vol. i. 359 *et seq.*; and Hasenclever, Chem. Ind. 1899, 25). A modified Maletra furnace suitable for blende is the Delplace (Lummen, Chem. Tr. J. 1916, 255, 261). A very large number of mechanical calciners, differing in detail, have been described. In Europe the Rhenania, Delplace and Spirlet are most usually employed, in America the Spence and Hegeler. The Wedge furnace is also used. The Spirlet furnace (Eng. and Min. J. 98, 617) has been installed in several large works. It appears that the working costs are more advantageous than those of the Hegeler (Hommel, Metallurgie, 1912, 281).

Of mechanical furnaces for roasting blende, Matthiessen and Hegeler's furnace has been worked successfully for a number of years in America at La Salle. It is a combination of Eichorn and Liebig's burner, with a stirring arrangement similar to Spence's. Hasenclever states that mechanical blende burners have not made much progress in Germany owing to the fact that the ores used contain lead and sinter when roasted, sticking to the moving parts and causing frequent stoppages (J. Soc. Chem. Ind. 1911, 1291). The blende furnace of Merton and Ridge is so arranged that the ore is moved forward on a long hearth by revolving stirrers. This furnace admits a much more thorough turning over of the ore than any other type. Heated air is passed into the bottom muffle, which achieves complete roasting of the blende. Each furnace requires a driving power of about 6 h.p. and one man can attend to four furnaces (J. Soc. Chem. Ind. 1917, 676; Met. and Chem. Eng. 17, 215; Eng. Pats. 13625, 1909; 3843 and 83981, 1911). Various types of roasting furnaces are described by Schapira (Chem. App. 1921, 8, 41, 51).

Furnaces for galena.—The gases from the roasting of galena or lead sulphide by the Huntington-Heberlein process are now used for sulphuric acid manufacture in several places in Germany; the working of these converters is intermittent, and a fairly continuous gas current can only be obtained by working a large number of converters charged at regular intervals. The Dwight-Lloyd furnace works continuously and can be made to deliver a regular gas current of 4–6 p.c. SO_2 by separating continuously the rich from the poorer gases and about 90 p.c. of the sulphur can be utilised for sulphuric acid manufacture (Hasenclever, *l.c.*).

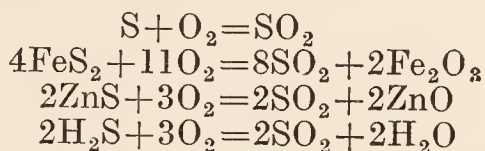
Spent oxide of the gas works is usually burnt in a special kind of shelf burner (Hill's burner) of the Maletra type. MacDougall's furnace with four chambers only has also been used for a number of years for burning this material, and latterly a modification of the Herreshoff burner

with three shelves has been introduced very successfully for this purpose.

The Harris mechanical furnace (Eng. Pats. 23331, 1910, and 25142, 1911) for roasting spent oxide (it is also used for pyrites) has special dust-trapped openings for discharging the oxide from bed to bed; it is said to require no dust-chamber (Chem. Trade J. Jan. 25th, 1913, 99, also 1914, 182). Furnaces for burning spent oxide have been devised by Wyld (Eng. Pat. 5751, 1911), Kershaw (Eng. Pat. 108986), and Crowther (Eng. Pat. 145366; J. Soc. Chem. Ind. 1920, 570 A).

Burners for sulphuretted hydrogen.—Sulphuretted hydrogen, as obtained from ammonium sulphate works, may vary greatly in composition, and always contains a large amount of carbon dioxide; it is frequently burnt in conjunction with spent oxide in ordinary oxide burners or even in pyrites burners. As obtained from alkali waste in the Chance process, its composition is much more uniform, and it may be burnt by itself in a brick chamber provided with baffling walls which help to keep up the heat of the burner and also to mix the gases thoroughly and so ensure perfect combustion.

The burner gas.—The quantity of air necessary for the complete combustion of sulphur in the different materials used for vitriol manufacture will vary considerably with the nature of those materials. Thus for free sulphur, pyrites, zinc blende, and sulphuretted hydrogen, the following equations represent the chief reactions taking place:—



which indicate that for a given weight of sulphur converted into sulphur dioxide the quantities of oxygen or air requisite will be in the proportion of 8, 11, 12, and 12 respectively. In addition to this, oxygen is required to convert the sulphur dioxide to sulphur trioxide, and a further excess is necessary to ensure the satisfactory working of the process. In the case of brimstone it is usual to employ such a surplus of air as will, after all the sulphur dioxide is oxidised and condensed, leave 5 p.c. oxygen in the exit gas, which corresponds to the following composition of the burner gas—

$$\begin{aligned} \text{SO}_2 &= 11.23 \\ \text{N} &= 79.00 \\ \text{O} &= 9.77 \\ \hline &100.00 \end{aligned}$$

For spent oxide no definite figures can be given, owing to the varying quantity of organic matter present.

For pyrites opinions differ as to the excess of oxygen required; Lunge considers 6.4 p.c. in the exit gas as about the proper amount, and the same for blende. Taking this figure the theoretical composition of the burner gases would be—

From pyrites	From zinc blende
$\text{SO}_2 = 8.59$	$\text{SO}_2 = 8.12$
$\text{N} = 81.54$	$\text{N} = 82.19$
$\text{O} = 9.87$	$\text{O} = 9.69$
<u>100.00</u>	<u>100.00</u>

(Lunge-Cumming, vol. i. 460).

In addition to sulphur dioxide a certain amount of sulphur trioxide is always formed when these substances are burnt. In laboratory experiments with brimstone, Lunge found that 2.48–2.8 p.c. of the sulphur is obtained as sulphur trioxide, and 5.05 p.c. in the case of pyrites. In the latter case, the increased proportion is doubtless due to the catalytic action of the oxide of iron present, for if the gases be passed over a layer of hot ferric oxide, the percentage of sulphur trioxide may be largely increased. The author has found about 6 p.c. of the sulphur present as sulphur trioxide in the gases, both from lump burners and from smalls burnt in Herreshoff furnaces. From each lump ore burner the percentage may vary from 2 p.c. when the charge is freely burning and the sulphur dioxide is at its maximum, to 20 p.c. when the sulphur dioxide is a minimum and the charge is almost completely burnt. Lunge states that in blende roasting gases he has found as much as 25 p.c. of the sulphur present as sulphur trioxide. The presence of this sulphur trioxide affects the above-mentioned figures for the theoretical burner gas by reducing the percentages of sulphur dioxide and oxygen, and a further alteration is caused by the fact that the burnt ore contains some sulphates of iron and copper, which will also reduce the oxygen content slightly and increase the nitrogen, and also a little ferrous sulphide, the presence of which will have the reverse effect.

In practice brimstone burner gases generally contain from 10–11 p.c. sulphur dioxide, and the gases from rich pyrites 7–8 p.c. sulphur dioxide.

Analysis of the burner gas.—Generally the process is controlled by determining the sulphur dioxide in the burner gas, and the oxygen in the exit gas. For the sulphur dioxide Reich's method is usually employed: a tube is inserted in the burner flue and the gas is aspirated slowly through a solution containing 10 c.c. *N*/10 iodine solution in 50 c.c. water, together with a little starch and sodium bicarbonate until the blue colour of the iodide of starch is discharged; the volume of water run out from the aspirating bottle + 11 c.c. for the sulphur dioxide absorbed gives the volume of burner gas used from which the p.c. of sulphur dioxide may be calculated or taken from the following table (Lunge's Technical Chemists' Handbook, 117).

Volume of gas aspirated	P.c. SO ₂ by volume	Volume of gas aspirated	P.c. SO ₂ by volume
82	12	128	8
86	11.5	138	7.5
90	11	148	7
95	10.5	160	6.5
100	10	175	6
106	9.5	192	5.5
113	9	212	5
120	8.5		

Raschig (Zeitsch. angew. Chem. 1909, 1182, states that the addition of sodium acetate prevents nitrous acid from interfering with the iodine test for SO₂.

For the determination of oxygen the gas is first treated with caustic soda or potash to absorb any acid vapours or carbon dioxide present, and then the oxygen may be absorbed by phosphorus, alkaline solution of pyrogallol or ammoniacal cuprous chloride in an Orsat or similar apparatus.

Alkaline pyrogallol absorbs oxygen very rapidly only a few minutes being required for each test, but the solution does not keep well. With phosphorus about half an hour is required, and the temperature must be kept above 16° . Below that temperature the absorption is very slow. The phosphorus is employed in the form of thin sticks or beads, and is always kept under water except during its exposure to the gas which is being tested.

If the total acidity of the gas is to be determined a standard solution of caustic soda is employed with phenolphthalein as indicator. This will give the $\text{SO}_3 + \text{SO}_2$ (Lunge, J. Soc. Chem. Ind. 1890, 1014). If the ore contain much organic matter, as when coal brasses or spent oxide are burnt, the carbon dioxide present will render this method inaccurate.

Comparison of brimstone and pyrites for sulphuric acid making.—The advantages of using brimstone are—

1. About $\frac{1}{3}$ less chamber space is required when burning brimstone.
2. The burners give less trouble in working and require less labour.
3. The acid obtained is much purer than pyrites acid, being free from arsenic and iron.

But these advantages are mostly more than counterbalanced by the fact that in most countries pyrites-sulphur only costs about half the price of brimstone, and that for some of the largest applications of sulphuric acid (*e.g.* the manufacture by the Leblanc process of saltcake or crude sodium sulphate for glass-making and alkali-making, the preparation of superphosphate, ammonium sulphate, and artificial manures generally) the impurities in pyrites acid are of little or no importance.

For manufacturing articles of food, for storage batteries and certain other purposes, these impurities are harmful, and there is still a certain amount of brimstone acid made in this country for these purposes, but it is gradually being displaced by purified pyrites acid from which the arsenic has been eliminated by precipitation as sulphide and filtration, and by acid made by the contact process in which the burner gases have to be purified to such an extent that an acid is obtained quite equal to brimstone acid in purity. Acid made from spent oxide of gas works, being practically free from arsenic, is also used in many cases in place of brimstone acid.

In America (where the disproportion between the price of brimstone and pyrites suitable for vitriol-making is, in many localities, not so great as elsewhere) the manufacture of brimstone acid is still carried out to a considerable extent, but even there during the last few years the use of pyrites and other sulphur ores has enormously increased.

Apparatus for introducing nitrogen oxides.—There are two chief ways in which the nitrogen oxides are introduced into the burner gas. In the first, nitric acid is evolved from a mixture of sodium nitrate and sulphuric acid introduced at intervals into an iron pot placed in the hot burner gas flue; whilst in the second, nitric acid is introduced in the liquid form either in the Glover tower along with the nitrous vitriol or into the first chamber.

Opinions differ as to the relative advantages

of the two methods, the potting system being mostly in favour in Great Britain, whilst Continental manufacturers more often employ the liquid acid method. The points in favour of the latter are the following: A more uniform introduction of the nitric acid vapours is possible than in the potting system, the admission of 'false' air, which takes place when the pots are charged or discharged, is avoided, and if at any time an extra supply of nitrogen oxides is temporarily required it can be instantly procured by increasing the rate of flow of the nitric acid. On the other hand, the use of liquid acid involves extra cost in distilling the acid, and more outlay for labour, carböys, and appliances for introducing it into the process, and when introduced into the chamber it may cause corrosion of the lead if not completely vaporised before reaching the bottom; this danger, however, is completely avoided by introducing it into the Glover tower.

The nitre pot system as first applied to brimstone burners was carried into effect by placing the cast-iron pots containing the mixture of nitre and sulphuric acid on the floor of the burner. As, however, they frequently frothed over and damaged the burner, they are now always placed in an extension of the latter where they are heated by the hot burner gases.

With pyrites burners the pots are usually placed in a separate nitre oven, practically an enlargement of the flue just beyond the last kiln with a door in front for introducing them and withdrawing them by means of a stout fork. The bottom is protected by a cast-iron tray to catch boilings-over, and the pots are charged at regular intervals in order to keep as equable a supply of nitrous vapours as possible. Every time the oven door is opened much air gets into the flues, and much gas escapes, and to avoid this the following arrangement is now frequently employed. There are usually two pots, each large enough to hold $\frac{1}{2}$ cwt. of nitre; they are fixed in the flue, and each is provided with a tubular spout at one end, which is plugged up when in use, and projects outwards from the oven. From 7 to 14 lbs. of nitre are charged into the pots alternately at regular intervals through a small hopper in the top of the oven, and a slow stream of sulphuric acid is run on to it by means of an S-shaped tube from a small tank provided with a stop-cock to regulate the rate of flow, so that a steady stream of nitric acid is liberated during each interval of charging; when about 56 lbs. of nitre have been worked off, the outlet plug is removed, and the fused nitre cake (acid sodium sulphate often designated Sally Nixon, *i.e.* sal enixon) is allowed to run out into a cast-iron saucer where it solidifies.

When the liquid acid method is employed, if there is no Glover tower the acid is introduced into the first chamber (usually a small preliminary one), being made to run intermittently or regularly over some distributing arrangement, exposing a large surface; such as a tall pyramid of glass or stoneware dishes or cylinders of such dimensions that the whole of the acid is volatilised before it reaches the lowest dish, which, however, should be provided with an overflow pipe to take away any acid which escapes vaporisation out of the chamber in order to prevent serious corrosion of the lead.

The acid may be introduced at a uniform rate by means of a Mariotte's bottle in which a constant pressure of liquid is maintained by only allowing the air to enter by a tube reaching down to within a short distance of the outlet.

Another method is to spray the acid into the chamber by a steam jet analogous to the arrangement used by Sprengel for spraying water. The best and simplest method is, however, to feed the acid in along with the nitrous vitriol and chamber acid at the top of the Glover tower; for although at one time it was thought that this mode of supply was likely to cause a loss of nitre, experience has shown that there is no increase in the consumption when this method was substituted for the cascade system (Lunge).

Where the sulphuric acid is intended for the manufacture of saltcake or superphosphate the nitric acid is sometimes introduced as a solution of nitre in water or dilute sulphuric acid, either by spraying into the chambers or running through the Glover tower. In the chamber there is the danger that it may reach the bottom acid undecomposed and cause corrosion, whilst stoppage from crystallisation of solid sodium sulphate is apt to occur when it is used in the Glover tower. To avoid this disadvantage a small intermediate tower has been suggested (Eng. Pat. 103877, 1916).

Occasionally the chambers are fed with nitrous gases obtained as by-products. Lunge states that at the Uetikon works near Zurich nearly all the nitre required for the chambers is obtained in the manufacture of ferric sulphate (iron mordant) by treating ferrous sulphate with nitric acid.

A feature which is likely to displace the older methods is the utilisation of the catalytic oxidation of ammonia. Plants of large capacity for the production of nitric acid have been erected in most countries. One form of converter is described by Partington (J. Soc. Chem. Ind. 1918, 337 R); also Schuephaus (Metall. und Erz. 1916, 13, 4, 21; Engineering, 1916, 102, 440; Chem. Tr. J. 62, 181). The analytical control of the plant is described by Taylor and Davis (J. Soc. Chem. Ind. 1918, 54 A, 465 A; Chem. Tr. J. 1916, 2, 413; 1917, 2, 259, 299, 319). See also Imison and Russell, (J. Soc. Chem. Ind. 1922, 37 T). An illustration of plant for this purpose is given in vol. iv. p. 598 of this Dictionary.

Two graphs are given by Cooper (Chem. Age. Lond. 1922, 6, 826) in a discussion on the relative costs of ammonia oxidation and nitre potting, from which it is possible to calculate the percentage saving possible under various market prices of nitre, sulphuric acid and ammonia.

The lead chambers.—These are usually placed at a considerable height above the ground, and are supported on brick or stone walls or piers, or on pillars of wood, or cast-iron columns. The space below can be used for storage purposes, or even for the pyrites kilns if high enough. On these piers or walls are placed stout wooden beams which carry the traverse joists which support the chamber bottom. These joists project several feet beyond the chamber frame in order to allow for passages between and around the chambers, and they are covered with a smooth wooden floor. In some cases the

beams are arranged from pier to pier across the width of the chamber and the joists then run in a longitudinal direction. Upon this floor the chamber frame is erected. The sides consist of two stout horizontal rectangles of wood, the sole-tree or sill, and the crown-tree or capping, connected by uprights or standards, which are mortised into them, and further tied by cross rails or stays. The crown-tree carries the transverse joists to which the roof of the chamber is attached. American pitch pine is usually employed for this framework, and is the best timber for the purpose, and wherever acids are concerned.

The chamber itself is usually constructed of sheet lead of such a thickness as to weigh 6 lbs. per square foot, occasionally 7 lbs., especially for the first chamber of the series, which being the hottest is the most readily attacked. In America 5-lb. or even 4-lb. lead is sometimes employed. The sides and roof are attached to the wooden framework by means of lead straps which are nailed to the uprights or cross rails and to the roof joists, the nails having lead-coated heads to enable them better to resist corrosion. These straps are burnt to the sheet lead by the flame of a blowpipe burning hydrogen in compressed air, or coal gas may be used with compressed oxygen from a steel cylinder. Usually the sheets themselves are similarly fused together, but sometimes unfused rabbet joints are employed, made by folding the edges over and then beating down flat. The roof and sides are burnt together at the crown-tree, and sometimes the bottom is also fused to the sides so that the whole chamber forms one gigantic water- and gas-tight leaden box; but more frequently the sides are suspended like a curtain in a large flat dish made by turning up the edges of the bottom, for which 10 lbs. lead is usually used, 12 or 15 ins. or even to a greater height up to 2 ft. 6 ins. if much acid storage room is required, and the construction will allow it. This dish or saucer is always kept luted with acid when the chamber is at work, and the upstand is protected all round by a 1-in. board to resist the outward pressure of the acid.

In Great Britain the chambers are seldom roofed in, the tops sloping slightly from one side to the other to allow the rain water to run off into a gutter, but the sides are usually protected from the wind by light wooden or corrugated iron walls. On the Continent, however, where the variations in temperature from summer to winter are greater, they are usually completely enclosed in buildings. Wherever possible the lead should be kept clear of the wooden framework of the chamber in order to allow efficient air cooling, the lead being more rapidly attacked where it is in contact with the wooden uprights, joists, &c. At some places the chamber frame is made of angle iron. In the Moritz system of construction (Fr. Pat. 395694, 1908; Chem. Trade J. 1911, 493) a strongly built skeleton of iron encloses the chambers, which are suspended from overhead beams by tie rods attached to the walls by lead strips; the top of each chamber is arched to prevent the accumulation of dust and to avoid dead corners, and the floor rests on perforated sheet iron supported by brick columns; the upturned edge is also iron plate bent under the floor. The advantage claimed

for this system is the uniform cooling which takes place, and which prevents local corrosion such as ensues where a wooden frame is in contact with the lead. A later patent (Fr. Pat. 444474, 1912) describes a light iron framework for chambers, preferably circular, which supports the walls and facilitates the cooling of the chambers. Awe (*Zeitsch. angew. Chem.* 25, 2523) compares the systems of horizontal and vertical suspension and decides in favour of the former. Other methods are described: Kalinowsky (D. R. PP. 260991 and 265640); Hartmann (Eng. Pat. 17035, 1913); Harris and Thomas (Eng. Pat. 6026, 1915); Nemes (Eng. Pat. 24223, 1913), and Seeck (Eng. Pat. 16187, 1914).

Chambers are usually of rectangular shape, 100–130 ft. long, 20–30 ft. wide, and 16–25 ft. high. They have been constructed up to 300 ft. in length, where there is only one large chamber employed. Since the introduction of water spraying instead of steam the tendency has been to increase the height to 25–33 ft., and at the same time to make them narrower, not more than 20 ft. wide. At the Rhenania Chemical Works the top corners are cut off to suit the shape of the roof and avoid dead corners (Lunge). The annular chambers of Delplace (Eng. Pat. 5058, 1890) have been tried in several places, but do not seem to offer any advantages over those of the ordinary rectangular shape. Meyer's tangential chambers of circular or polygonal section (Eng. Pat. 18378, 1888) have been erected at a number of works on the Continent; the gas enters tangentially on the upper part of the sides, and the outlet pipes are in the centre of the bottom (*Chem. Ziet.* 1899, 297; *Zeitsch. angew. Chem.* 1899, 656; 1900, 739; 1901, 1245). Circular or polygonal chambers are also recommended by Lu Luttgen (D. R. P. 244402, 1910).

Notes on the construction and equipment of chamber plants are given by Donaldson (*Chem. Eng. Mining. Rev.* 1923, 15, 212).

Fairlie (*Chem. Met. Eng.* 1921, 25, pp. 861, 917, 964, 1005), in an illustrated article, deals with many features of the chamber process. The numerous data and facts are likely to be of great utility to the chemical and engineering staff engaged in erecting plant.

In England all the chambers are generally of equal size, three or four forming a set and taking the gas from one set of kilns; or five or six chambers may be combined and take the gases from two sets of burners, the fifth and sixth being common to the two sets; but in France one large chamber is frequently employed with small ones before and behind it. Hasenclever (*Chem. Ind.* 1899, 26), at the Rhenania Works, combines two large chambers with two small back ones, whilst other manufacturers prefer three chambers in series decreasing in size from the first to the last.

The capacity of each chamber varies between 25,000 and 70,000 cub. ft., but occasionally they may be constructed as low as 10,000 cub. ft., or as high as 140,000 cub. ft. The total capacity of a set is seldom more than 200,000 cub. ft., but Hasenclever mentions the existence of sets of 420,000 cub. ft. capacity. The average capacity will probably be between 100,000 and 150,000 cub. ft. Fairlie (*Met. and Chem. Eng.* 1918, 82)

describes two large plants of 4,000,000 and 2,250,000 cub. ft. capacity, producing daily 300 tons of 60°B. acid. Mathewson (*Eng. and Min. J.* 1915, 723) gives an account of the Anaconda plant. Meyer's tangential chambers are usually about 33 ft. in diameter and 26 ft. high, and are combined in sets of three (66,250 cub. ft. total capacity). Falding (*Eng. and Mining J.* 1909, 441; also 1913, 318; U.S. Pat. 932771, 1909) recommends the use of one large chamber of such a height that its vertical axis is in the proportion of 3 to 2 over any horizontal axis. Some of the difficulties of construction are overcome by the use of reinforced concrete framework (*J. Soc. Chem. Ind.* 1909, 1086). Small chambers require more lead and occupy more space than large ones of equal capacity, and it is taken as a practical rule that for every cubic foot of chamber space there should be about 0.2 sq. ft. of total surface (top, bottom, sides, and ends). See also *Zeitsch. angew. Chem.* 1911, 717; *J. Ind. Eng. Chem.* 1913, 223; Hoffmann, *Chem. Zeit.* 1913, 1271; Fairlie, *J. Ind. Eng. Chem.* 19, 404; Channing, *Chem. Abst.* 1913, 541; *J. Soc. Chem. Ind.* 1908, 6677.

The different chambers of a set are sometimes arranged so that each is a few inches higher than the preceding one in order to enable the weaker acid produced in the last chamber to be run back into the stronger first chamber, and to get rid of traces of nitre which it usually contains. If the chambers are on the same level injectors are used for this purpose. Mills and Packard (Eng. Pat. 12069, 1913) employ chambers in the form of truncated cones with external water cooling. The very small chamber space of 3 to 5 cub. ft. per lb. of sulphur charged is required. De Lummen (*L'industrie chimique*, 5, 33) gives a description of this system. Reference to this type of chamber will also be found in *Chem. Tr. J.* 1915, ii. 131; Fairlie, *Chem. Met. Eng.* 1921, 24, 786; also Breton, *Chim. et Indus*, 1922, 7, 253. Dior (Eng. Pat. 164572, 1920) recommends chambers of an inverted funnel shape, decreasing in size from Glover to Gay-Lussac tower. Sonneck (Eng. Pat. 164627, 1920) describes a form of tower-like chambers. Kaltenbach (Eng. Pat. 159156, 1920) suggests replacing chambers by a series of parallel tubes, water-cooled and filled with a suitable packing material; and Piperaut (Eng. Pat. 163030, 1921) aims at similar results by means of small chambers connected by cooling pipes. A series of packed cells are described by Larison (*Chem. Met. Eng.* 1922, 26, 830), who substitutes acid-proof masonry towers filled with a brick grillage or 'packed cells' for the lead chambers. A strong circulation of acid in process is maintained, which is artificially cooled. He claims a saving of 40 to 50 p.c. on the cost of an equivalent lead chamber plant, the ground area is only 30 to 40 p.c., the operating cost is no greater, and the plant can be started up in a much shorter time. Details of cost and operation are given.

The connections between the chambers may be circular or rectangular in section, and are usually constructed of 10–12 lb. lead, those of the latter shape being supported by a wooden frame-work, whilst the round pipes are held in

position by means of iron hoops with wood laggings. Considerable difference of opinion exists as to where they should leave and enter the chambers, some being of opinion that the gases should leave each chamber near the top and enter the next near the bottom, while others prefer the reverse arrangement. According to Lunge and Naef's experiments, it is a matter of indifference where the connecting tubes are placed, but Porter (J. Soc. Chem. Ind. 1902, 476), after describing some experiments with a glass model to show the path which gases travel in the chamber, recommends that they should enter near the bottom and leave near the top of each chamber.

There is a certain definite relationship between the total cubic capacity of a set of chambers and the quantity of acid produced in a specified time. The number of cubic feet of chamber space required for condensing the acid from 1 lb. of sulphur burnt in 24 hours (the form in which it is usually expressed in England) will depend on a number of different factors. It will be less for brimstone than for pyrites, owing to the difference in the composition of the burner gas; it will be less for rich pyrites than for poor for a similar reason; other things being equal it will depend on the proportion of nitre used, a larger consumption compensating for a smaller chamber space; it will also depend on the presence or absence of Glover and Gay-Lussac towers, and likewise on the size and efficiency of those towers. It will be less in winter than in summer, owing to the lower temperature and increased density of the gases in the colder season, and it can be reduced by a number of different arrangements for cooling the gases and the chambers, which will be referred to later.

The coefficients of radiation, *i.e.* the calories radiated per hr. per sq. m. of surface per unit temperature difference for lead chambers in a wooden framework are estimated to be for the bottom 1, for the top 3, for the sides 6, and for the connections 12. The wooden framework reduces the effective surface by 8–10 p.c., and the coefficients of radiation for a steel frame chamber are therefore increased by this amount. This is the principle of the "Nevers," and other types of high rectangular or round chambers, which are described in detail. The system of continuous strapping to a metal framework suspended from above obviates all strap repairs. Other methods proposed for increasing radiation, such as the use of internal agitators and the provision of water cooling, are in the author's opinion nullified by the additional first cost and running expenses entailed. The provision of sprays of cooled and diluted chamber acid in place of the usual water sprays, however, gives promise of accelerating the reaction, the slow radiation from the chamber walls being supplemented by the efficient working of a cooling coil. An economy in nitre is also obtained (J. Soc. Chem. Ind. 1924, 43 B, 785).

Generally speaking, where Glover and Gay-Lussac towers are not used, 25–30 cub. ft. of chamber space per lb. of sulphur burnt per 24 hours will be required. If moderate-sized towers are used 16–20 cub. ft. will be sufficient, and by increasing the size of these towers it may be reduced to 10–11 cub. ft., as in the

intensive system, but in the latter case the wear and tear of the chambers will be very considerable, unless steps are taken to keep the temperature in them from rising too high. The working of the process also requires more supervision. These figures are for pyrites; for brimstone the chamber space need only be about 75 p.c. of the above figures.

On the Continent the number of kilogrammes of H_2SO_4 produced per cubic metre per 24 hours is the form in which the chamber space is expressed.

Opinions differ among manufacturers as to how long it is possible to work a chamber economically. Generally speaking after 10 years' work the repairs required to keep a chamber in good working order are very considerable, and many are of opinion that it should then be rebuilt, losses through leakages, injury to the frame work, and cost of patching will more than counterbalance the cost of re-erection. On the other hand, where chambers are well constructed and the process is well controlled and not forced, they have been known to last 20 or even 30 years, with occasional stoppages for repairs after the first 8 or 10 years. The length of the serviceable life of a chamber is dependent upon its position in the series. A last chamber may be serviceable for 25–30 years, a first chamber, however, will probably require to be rebuilt after 8–10 years' working. Intensive working and the presence of fluorides in the pyrites are usually responsible for excessive corrosion of the chambers. Under tropical conditions the corrosion is severe and output diminished. One observer has reported a decrease in yield from 91.4 p.c. in the cool season to 86.6 p.c. in the summer, accompanied by a large increase in the rate of corrosion. The correlation of corrosion and the nature of the lead used in chamber construction is dealt with by McKellar (J. Soc. Chem. Ind. 1921, 40, 137).

Burgemeister (Chem. Zeit. 13, 1633; also J. Soc. Chem. Ind. 1890, 66) has made various measurements of the rate of diminution in thickness of the lead in a set of two chambers, one of which had lost 26.8 p.c. after working 210 months, and the other 17.65 p.c. of its thickness after 120 working months. The latter was a small chamber placed between the Glover and the large chamber first mentioned, and kept at a higher temperature.

Arrangements for supplying steam or water to the chambers.—When no Gay-Lussac and Glover towers are used all the water ultimately transformed into chamber acid must be supplied in the form of steam or water spray. If the strength of the chamber acid is $120^\circ\text{Tw.} = 68.7$ p.c. H_2SO_4 , 1.96 parts of water will be required for each part of sulphur burnt; if towers are employed, and the average strength of the acid obtained is $145^\circ\text{Tw.} = 79.25$ p.c. H_2SO_4 , the water required will be equal to 1.44 times the sulphur burnt.

This is usually introduced into the chambers in the form of steam generated in an ordinary steam boiler. At one time this was sometimes mounted on the burners so as to utilise the heat of combustion of the pyrites, but this arrangement has been given up everywhere since the introduction of the Glover tower. The pressure required need not be more than sufficient to

carry the jets of steam well into the chamber, say 5–10 lbs. per square inch, but is very important for the regular working of the process that it should be kept uniform; to ensure this, automatic regulators are employed in some works to keep a uniform pressure in the steam main, no matter what the boiler pressure may be. The exhaust steam of engines may be utilised for supplying the chambers, provided that they are worked in such a way as to leave a definite pressure in the exhaust.

Practice differs considerably in different countries, and amongst different manufacturers, as to the method adopted for introducing the steam so as to mix uniformly with the burner gases. In England frequently only one jet is employed for each chamber, placed somewhere near the inlet pipe or a little above the centre of the chamber end, but on the Continent the practice is to employ a number of jets at right angles to the direction of the gaseous current either in the long chamber sides near the top, or through the roof of the chamber. The regulation is certainly much simpler and easier in the former method, but the distribution of the steam cannot be so well controlled as in the latter. Where a Glover tower is used the first part of the first chamber requires little or no additional steam to that entering with the gases, and therefore the first steam jet should be some distance from the front end of the chamber. Jets introduced at the far end in opposition to the direction of the gaseous current are sometimes employed, but tend to impede the draught.

In 1873 Sprengel patented the employment of pulverised water, *i.e.* water reduced to a mist-like spray by blowing a jet of steam at about 2 atmospheres pressure through a platinum nozzle in the centre of a water jet; with a properly proportioned compound jet, 4 parts by weight of water can be converted into fine spray by 1 of steam. The spray does not carry as far as a steam jet, wherefore in a large chamber a number of jets are necessary, and are placed in the sides about 40 ft. apart, and supplied with water from a tank fixed at some height above. The advantages claimed for the use of spray instead of steam are, that not only is fuel saved, but the temperature of the chamber is lowered so that more acid can be produced in a given chamber space. Sprengel's apparatus was worked for a number of years at Barking, but was given up on the introduction of Glover and Gay-Lussac towers there, and has practically gone out of use.

On the other hand, pulverised or atomised water (produced by the mechanical action of a fine stream issuing under a pressure of 2 atmospheres from a platinum nozzle on to a platinum button) has been successfully applied for a considerable number of years at Griesheim (Lunge), and has lately come into more general use where the intensive system of sulphuric acid manufacture is worked. Two rows of water jets, 20 ft. apart, are introduced through tubes in the chamber tops, and the water has to be specially filtered to avoid blocking up the fine jets used. The Berk spray, resembling the usual impinging jets of an acetylene burner in design, is a satisfactory form of apparatus. For narrow chambers only one row of jets is employed. Where the intensive system is

worked the use of atomised water has been of great service in keeping down the temperature of the chambers, and so preventing rapid wear and tear and excessive nitre consumption. Kestner (J. Soc. Chem. Ind. 1903, 334) gives the following calculations showing the effect of replacing steam by water sprays:—

Heat of formation of $\text{H}_2\text{SO}_4 + 3\text{H}_2\text{O}$ (approx. chamber acid) . . .	=65,500 Cal.
Heat given up by condensation of steam at 120° to 60° . . .	=41,976 „
Total heat . . .	=107,476 „

If the steam is replaced by water at 15°—	
Heat of formation of $\text{H}_2\text{SO}_4 + 3\text{H}_2\text{O}$	=65,500 Cal.
Heat absorbed by water raised from 15° to 60° . . .	=3,240 „
Total heat . . .	=62,260 „

The difference in the two cases is thus 45,216 calories.

If the average strength of the acid produced is represented by $\text{H}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$, which will more nearly represent the correct strength when the Glover tower acid is taken into consideration, the difference in the heat of the reaction will be=33,910 calories. Water sprays cannot entirely replace steam, which is usually required in the last chamber, and also in the other chambers in very cold weather in order to prevent the temperature falling below a certain minimum, which Benker considers should be 60°–65° for the first chamber (Kestner, J. Soc. Chem. Ind. 1903, 334). For this reason water spraying is of very little use in non-intensive working, except in very hot weather.

A special platinum jet for converting water or acid liquids into spray has been constructed by Benker in which the distance between the nozzle and the disc is adjustable, the disc being moved backwards and forwards by a rod at the end of which is cut a fine thread which works in a similar nut above. The jet is easily cleaned.

Korting Bros. have introduced a spray producer which gives the liquid a rotating movement, so that, issuing from the jet, it is projected in a conical spray. The nozzle is of platinum usually, but it can be replaced by a glass jet fitted into a hard lead nozzle by a small india-rubber washer. These spray producers have proved very successful, and have been used for a number of years in Continental factories (Lunge) (Harkort, D. R. P. 275388, 1913; Nagel, Zeitsch. angew. Chem. 1912, 1220). Szigeti replaces platinum by tantalum nozzles (Nagel, J. Soc. Chem. Ind. 1914, 322; Norton, J. Ind. and Eng. Chem. 1912, 532).

Guttman (Eng. Pat. 18927, 1906) has patented the spraying of acid from the back chambers into the first and second chambers instead of steam or water; stronger chamber acid is obtained, and no harm is done if the spraying apparatus is defective.

Raschig (J. Soc. Chem. Ind. 1911, 172) has also suggested the spraying of weak sulphuric acid into the chambers instead of water, so as to avoid the possible reduction of the higher oxides of nitrogen to nitrogen monoxide or nitrogen. Scrubbing of the final exit gases and spraying this into the chambers might prove of utility (J. Soc. Chem. Ind. 1917, 136).

The quantity of steam or water spray introduced into the chamber is regulated so as to produce an acid of a definite strength; and drips or tell-tales consisting of earthenware or leaden trays are placed inside the chambers to catch a certain amount of the condensing acid which runs through a tube into a lead or glass cylinder outside the chamber, and can there be tested from time to time; or samples can be obtained of the acid condensing in the connections between the chambers and tested at intervals in the same way.

In order to draw off acid from a chamber, a small leaden box is placed on the floor close by, open at the top, and of the same height as the upstand of the chamber bottom, and is connected at or near the bottom with the chamber by means of a pipe. In the bottom of this box is a seating of regulus metal (a hard alloy of lead and antimony) closed by a plug; on lifting this plug the acid in the box runs away through a pipe attached to the seating, and at the same time more acid levels into the box from the chamber. By allowing the acid to enter the box through a seating which can be closed by a plug, the same box may be used for two or more chambers. Another method is to siphon the acid from the chamber into the box by a siphon with a cup attached at each end in order to keep it always full when not in use, so that it starts to act as soon as one limb is put into the acid.

Arrangements for production of draught.—The draught necessary for moving the acid gases through a set of chambers may be produced in several ways. In the first place, the hot burner gases are lighter, bulk for bulk, than air at the ordinary temperature, and consequently tend to rise and produce an indraught at the burners and a pressure in the chambers. The hotter the gases, and the higher they have to rise before they enter the Glover tower or chambers, the greater will be the draught due to this cause. At the end of the system the outlet pipe is usually connected with a chimney which assists in drawing the gases through the chambers, or else the outlet consists of a vertical pipe from the last chamber or tower; this has a slight aspirating action, owing to the exit gases being lighter than the air, which may be increased by means of a simple jet of steam, or better, by a Korting's injector. The formation of sulphuric acid itself in the chambers also acts as a cause of draught, the volume of the gases being reduced by the amount of condensation taking place.

For the regulation of the draught dampers are usually provided between the burners and the chambers, and in the outlet pipe at the end of the system.

Where a chimney is employed, any great variations in the draught from this may be corrected by a damper or throttle valve, which is automatically worked from a lever, on the other end of which hangs a bell standing in an annular lute containing water or other suitable liquid. The air in the bell is connected with the exit pipe beyond the damper, so that, when the draught from the chimney increases the bell descends in the lute, thus causing the other end of the lever to rise, partially closing the damper; the reverse happens when the draught decreases. Latterly the employment of fans

for producing the necessary draught by mechanical means has very largely increased. These are usually made of iron covered with lead, of antimonial lead or of stoneware, and are generally placed between the last chamber and the Gay-Lussac tower, or if there are two of the latter towers, between them (Kestner, *J. Soc. Chem. Ind.* 1903, 334; Benker, *Zeitsch. angew. Chem.* 1903, 861). They have also been placed between the Glover tower and the first chamber, but lead or antimonial lead is rapidly corroded there (Niedenführ and Lüty, *ibid.* 1902). Falding employs two fans, one behind the Glover tower to regulate the draught of the burners, and the other in front of the Gay-Lussac (*Min. Ind.* vii. 672).

Mühlhäuser (*Zeitsch. angew. Chem.* 1902, 672) describes the history of introduction of the fan; see also Rabe (*ibid.* 1905, 1735), and Schliebs (*ibid.* 1905, 1900).

O'Brien places a cast-iron fan immediately behind the burners before the nitre oven and Glover tower. The temperature inside the fan is 540°, and it is covered with a 1-in. coat of asbestos cement; water is used as a lubricant instead of oil (Falding, *Min. Ind.* ix. 621). The actual volume of gas passing through the chamber system may be determined by measuring the speed of the gaseous current in the connecting pipes or exit pipe by means of Fletcher's or Swan's anemometer.

Wrought-iron fans have also been employed to impel the burner gases (Thede, *Zeitsch. angew. Chem.* 1918, 2). Heinz (U.S. Pat. 1057149) claims that the pressure and movement of the gases may be regulated by the admission of air to the chamber or conduits (D. R. P. 286972, 1913).

Guy-Lussac and Glover towers.—In 1827 Gay-Lussac proposed the use of a coke tower for absorbing the escaping nitrous fumes in strong sulphuric acid, but it was not until 1842 that the idea was put into practice, and it was not until some time after the invention of the Glover tower in 1860 that the Gay-Lussac came into general use. This delay was due to the fact that up to that date, all the acid used in the latter tower had to be concentrated, and the nitrous vitriol obtained could only be denitrated by dilution with water, so that the saving in nitre was partly counterbalanced by the cost of the fuel required for reconcentrating the acid. But the introduction of the Glover tower rendered this expense unnecessary, and at the present day there are very few sulphuric acid manufacturers who do not make use of these appliances.

The Gay-Lussac tower consists of a tall column, the walls of which are of lead, packed with some material, such as coke, which presents a large surface so as to bring the gas passing up through the tower into intimate contact with a stream of sulphuric acid entering at the top and passing down the tower. It is connected with the exit from the last chamber of a set, and receives all the gas leaving that chamber; this gas contains a large amount of nitrous vapours, which are absorbed by the descending sulphuric acid and are again introduced into the process.

The tower is usually built on a solid block of brickwork or on strong brick piers, sur-

mounted by an arch, or cast-iron columns may be employed, carrying a platform of iron bearers or rails. The brickwork or iron is protected from possible acid drips or leaks by sheet lead. The tower itself is constructed of sheet lead, supported by a wooden frame-work in the same manner as the chambers. Sometimes angle iron is used instead of timber for the frame. Square-sectioned towers are usually preferred, as being somewhat simpler to construct than round ones, but the latter have the advantage that for a given capacity less lead is required, and the gaseous current is more uniformly distributed within the tower. The sides are usually made of 8 or 10 lb. lead, and the bottom, which is turned up at the edges to form the upstand, of 12–18 lb. lead. The sides are not 'burnt' to the bottom, but dip into the acid, which forms a lute as in the chambers. The lower portion is usually lined with acid-proof blue bricks, put in dry without mortar or cement in order to protect the lead from being damaged by the packing. 1-in. splits are sometimes used to economise space.

The width varies from 4 to 10 ft., and the height from 30 to 50 ft., the dimensions depending on the capacity of the set of chambers.

The cubical contents should be at least equal to 1 p.c. of the chamber space, and may with advantage be increased to 2 p.c. when working with a normal chamber capacity of 16–20 cub. ft. per lb. of sulphur burnt per 24 hours. But when the chamber space is reduced to 10 or 11 cub. ft. per lb. sulphur, as in intensive working, the capacity of the Gay-Lussac tower is frequently increased to about 4 p.c. of the total capacity of the chambers. Two towers are usually employed in this case, and also with large sets in non-intensive working.

Sometimes the gases from a number of different sets of chambers, after leaving the Gay-Lussac towers, are passed through a large final absorbing tower in order to reduce the loss of nitrous vapours due to non-absorption to a minimum.

The pipe bringing the gases from the last chamber enters the side of the tower near the bottom, and just above is fixed the grating which carries the packing. This grating may consist of iron bars covered with lead, carried by the brick lining, or it may be of blue bricks on a series of parallel brick arches or of specially shaped acid-proof stoneware blocks. The packing itself used at one time almost universally to consist of hard-burnt furnace coke, which are still used to a very considerable extent, but owing to the fact that it is apt to disintegrate in the tower which it gradually blocks, and that it also has a slight reducing action on the higher oxides of nitrogen, it has been, to a certain extent, replaced by cylinders of acid-proof stoneware, specially-shaped bricks, Guttman stoneware balls, or Bettenhausen cones. When coke is used large lumps 12 or 14 ins. long are placed on the grating in regular layers, and the size of the fragments is gradually reduced as the packing goes on, until in the upper part pieces 3–4 ins. in size are employed. The desirable qualities of material for tower filling are summarised by Schobner (*Tonindustrie Zeit.* 1914, 1429). The chief of these are: (1) resistance to acids, &c.; (2) low sp.gr.; (3) least possible resistance to the passage of gases;

(4) greatest possible reaction surface. Solid spheres give 10 p.c. free cross-section, fill 74 p.c. of its volume, and have the smallest possible ratio of surface to weight. Other types of filling give: Vertical hollow cylinders 22 p.c. free cross-section, fill 44–45 p.c., free surface per cub. metre 40 sq. met., inverted basin 10 p.c., 50 p.c., 22 p.c.; rhombohedral grate bar 30–35 p.c., 40–45 p.c., and 25–50 p.c. A filling of inverted V's with fluted and perforated sides is held to be the most efficient (*Chem. Age*, Jan. 31st, 1920). Some information on the efficiencies of various types is given in *Chem. Met. Eng.* 1921, 24, 741. The top of the tower consists of sheet lead supported from above by iron bars covered with lead, and a large number of inlet holes for the acid are spaced over the whole area. Each hole has an upstanding rim, which is covered with a leaden cap which allows the acid to pass into the tower, but no gas to escape. The acid is conveyed to these lutes by leaden pipes from the bottom of a leaden box divided by radial partitions into sections which are continuously fed with acid by means of a reaction wheel or rotating distributor working on the principle of the Barker's mill. Another method of distribution is by means of an intermittent siphon, which at regular intervals flushes an intermediate leaden box from the bottom of which numerous pipes run to the lutes. The reaction wheel or siphon is fed with acid from an overhead tank, and the quantity passing down the tower is regulated by a tap. As it is of the utmost importance to the working of the process that this stream should be as uniform as possible, and since any variations in the level of the acid in the tank above will cause similar variations in the quantity the regulating tap will pass, various contrivances are employed for ensuring a uniform pressure of acid at the point of delivery. The most efficient of these is the balancing apparatus described by Lunge (*Sulphuric Acid*, vol. i. 599), in which the acid flows from the bottom of the tank into a smaller intermediate vessel on the same level in which a hollow leaden ball is suspended from the end of a lever. The entering acid presses the ball upwards, the other end of the lever descends and closes the outlet from the tank until sufficient acid has run out of the intermediate vessel to allow the ball to move down and open the outlet valve again. Thus the level of the acid in the small vessel will be independent of that in the main tank (*Mason, Chem. Zeit.* 1914, 800).

The acid is usually forced up to the top of the tower by means of compressed air from a strong cast-iron vessel which is sometimes lined with lead, but this is unnecessary, as acid of the strength used has very little action on cast-iron. These acid eggs, as they are called, hold several tons of acid. Latterly they have been replaced in some works by automatic elevators or pulsometers, which were first introduced by Harrison Blair, and have been considerably improved by Laurent and Kestner. They work continuously, and the rate of supply of acid to the towers can be regulated by the air-inlet cock below, so that no regulating arrangement or large storage tank is required on the top. When the tower is very high and the air pressure available is not sufficient to force the acid up to the top in a continuous stream, a modification

of the automatic elevator, known as an *Emulseur*, may be employed, in which a certain amount of air is allowed to mix with the acid as it is forced up, the emulsion of acid and air requiring less pressure to elevate it than the acid by itself.

T. Meyer (*Zeitsch. angew. Chem.* 1910, 972) recommends the use of multistage turbine centrifugal pumps of hard lead connected to an electric motor, which he states have an efficiency of 19·4 p.c. of the total energy supplied as against 3½ p.c. when compressed air is used.

Working the Gay-Lussac tower.—The acid used for absorption should be at least 144°Tw., and it will be more efficient if it is 150°–152°Tw.; it may readily be obtained of the latter strength from the Glover tower. It should also be as cool as possible, not above 30°C. Hot acid absorbs badly, and where coke is used for packing some of the higher nitrogen oxides may be reduced to nitric oxide. The quantity used per 24 hours should be at least equal to one-half the daily production of acid, and in many cases a quantity equal to the total daily make is used; in intensive working at least twice the daily production has to pass through the Gay-Lussac towers in order to prevent excessive loss of nitre.

These towers increase in importance the more intensively a plant is worked. A construction with horizontal internal walls with apertures designed to make the gases take a zigzag course is recommended. In some cases it may be desirable to introduce a small quantity of burner gas at the end of the chambers or to pass the exit gases from the Gay-Lussac tower through a tower fed with acid of *d* 1·65 to avoid the coloration of the exit gases by the higher oxides of nitrogen (*J. Soc. Chem. Ind.* 1924, 43 B, 785).

The nitrous vitriol running off from the bottom of the tower usually contains from 1 to 2 p.c. N_2O_3 ; it is a solution of nitrosulphonic acid or nitrosulphuric acid (chamber crystals) $SO_2(OH)(NO_2)$ in sulphuric acid, and it is decomposed on dilution with water, the N_2O_3 being liberated. The percentage of N_2O_3 depends on the quantity of acid run down the tower; if it contains above 2 p.c. N_2O_3 there is danger of loss from incomplete absorption. When the process is working regularly it is almost colourless, but when the exit gases contain an excessive amount of unoxidised SO_2 it turns dark purple owing to the reduction of the $SO_2(OH)(NO_2)$ to $SO_2(OH)N(OH)O$, called by Raschig nitrosi-

sulphonic acid, and appears full of bubbles of NO. It has been stated that some nitric acid is usually present in the nitrous vitriol, but Lunge holds that this is never the case under normal conditions of working. If such an excess of nitre be used that N_2O_4 exists in the gases leaving the last chamber, some nitric acid will probably be formed, but if the tower is packed with coke the latter will prevent this formation, and only where some non-reducing packing is employed is it likely that the formation of nitric acid will take place (*J. Soc. Chem. Ind.* 1885, 31). Lunge also controverts the statements of Benker and Lasne that when sulphur dioxide is practically absent from the gases entering the Gay-Lussac tower, the N_2O_4 present is not readily absorbed by the acid in the tower. To avoid this loss they proposed to introduce into the gases leaving the last chamber, a certain quantity of burner gas by means of a steam jet in order to reduce the N_2O_4 to N_2O_3 , which is more readily absorbed (*D. R. P.* 17154, 1881). Benker modified this at a later date (*D. R. PP.* 88368, 91260) by taking a small quantity of gas from the first chamber and injecting it into the last or into a special chamber between this and the Gay-Lussac tower. See also Fairlie, *J. Soc. Chem. Ind.* 1917, 196, 491.

Petersen (*D. R. P.* 226793, 1909) states that ferrous sulphate in the Glover tower acid hinders the absorption of nitrous acid in the Gay-Lussac tower, and recommends that the ferrous sulphate should be oxidised by the addition of a little nitrous vitriol to the absorbing acid for the last tower.

The quantity of N_2O_3 in the nitrous vitriol may be estimated by means of potassium permanganate. 50 c.c. of $N/2$ $KMnO_4$ solution are taken, diluted with five times its volume of water, and the nitrous vitriol is run in from a burette with constant stirring until the colour just vanishes. 1 c.c. $N/2$ $KMnO_4$ = 0·0095 gm. N_2O_3 .

If nitric acid is present it is not estimated by this method, but the total nitrogen compounds present may be determined by means of Lunge's nitrometer, in which they are converted into NO by shaking with mercury and the volume of gas produced can be measured. The following table represents the quantities of various nitrogen compounds in milligrams corresponding with 1 c.c. of NO at 0°C. and 760 mm. :—

	NO	N	NO	N_2O_3	N_2O_5	HNO_3	KNO_3	$NaNO_3$
1 c.c.	.	0·627	1·343	1·701	2·417	2·820	4·521	3·805
2 "	.	1·254	2·686	3·402	4·834	5·640	9·042	7·610
3 "	.	1·881	4·029	5·103	7·251	8·460	13·563	11·415
4 "	.	2·508	5·372	6·804	9·668	11·280	18·084	15·220
5 "	.	3·135	6·715	8·505	12·085	14·100	22·605	19·025
6 "	.	3·762	8·058	10·206	14·502	16·920	27·126	22·830
7 "	.	4·389	9·401	11·907	16·919	19·740	31·647	26·635
8 "	.	5·016	10·744	13·608	19·336	22·560	36·168	30·440
9 "	.	5·643	12·087	15·309	21·753	25·380	40·689	34·245

The Glover tower.—Before the invention of the Glover tower the methods used for decomposing the nitrous vitriol obtained from the Gay-Lussac tower in order to reintroduce the

nitrous compounds into the process were dependent on the use of hot water or steam, or else sulphur dioxide, dilution of the acid being necessary in both cases. The wear and tear of

the apparatus employed was always very considerable, and as only dilute acid was obtained, additional expense was incurred in concentrating the acid again for supplying the Gay-Lussac tower. This was sometimes done by means of evaporating pans placed on top of the pyrites, or sulphur burners, but owing to danger of leakages this method did not come into general use. The advantages of the use of the Glover tower over any other system of denitration are that the heat of the burner gases is utilised for restoring the nitrous vapours uniformly to the chambers, and also for supplying them with steam, and that the burner gas is cooled down to such a temperature that no cooling pipes are required, and the wear and tear on the first chamber is considerably reduced. Much of the heat evolved by the combustion of the sulphur is also utilised in concentrating the chamber acid.

Owing to the higher temperature of the gases Glover towers (Fig. 8) must be far more strongly built than Gay-Lussac towers, which in other respects they greatly resemble. The sides are usually of 14–18 lb. lead, and the bottom of 35-lb. lead, and the tower is lined with fire-bricks capable of resisting both heat and strong acid, or with volvic lava; this lining, which is put in dry without mortar of any kind, is about 2 ft. 3 ins. thick at the bottom, and decreases from 18 ins. above the grating carrying the packing to 4½ ins. at the top. The packing usually consists of flint, picked from the chalk, and washed with hydrochloric acid. This material has the advantage of being absolutely acid resisting, but it is very heavy, does not possess much surface, and is readily blocked up by dust. Other suggestions and modifications have been made to obviate the blocking of the tower and provide longer reaction spaces (Bithell and Beck, Eng. Pat. 28743, 1913; Hoefling, D. R. P. 281135, 1912). Acid-proof fireclay cylinders or bricks, either plain or dished and perforated, are frequently used instead, more particularly where pyrites dust burners are employed. They do not block up so readily, and also allow more free space in the tower for the reactions (Lüty, Zeitsch. angew. Chem. 1896, 645). Sometimes coke is used in the upper portion, but there is always danger of the coke firing should the acid feed be stopped for any reason. In America Herreshoff uses a particular kind of quartz rock, not only for the packing itself, but also for the grating supporting the packing, and for the lining; as the lumps of quartz are not obtained in very regular shape the space next the lead is packed with a thick layer of quartz sand; the lead is protected outside by iron plates (J. Soc. Chem. Ind. 1908, 269).

Volvic lava is largely used on the Continent both for lining and for packing Glover towers. In some cases the tower itself is made of this material without any leaden shell. The segments are held together by iron hoops covered with lead. There are no tanks on the top, as the tower is fed by means of automatic elevators from below.

The height of the Glover tower is generally much less than that of the Gay-Lussac tower, from 20 to 30 ft., while the width is proportionately greater, so that the cubic capacities of the two do not widely differ. A tower 9–10 ft. square and 25–30 ft. high containing 2025–3000

cub. ft. will suffice for a set of chambers containing 140,000–200,000 cub. ft. From 550 to

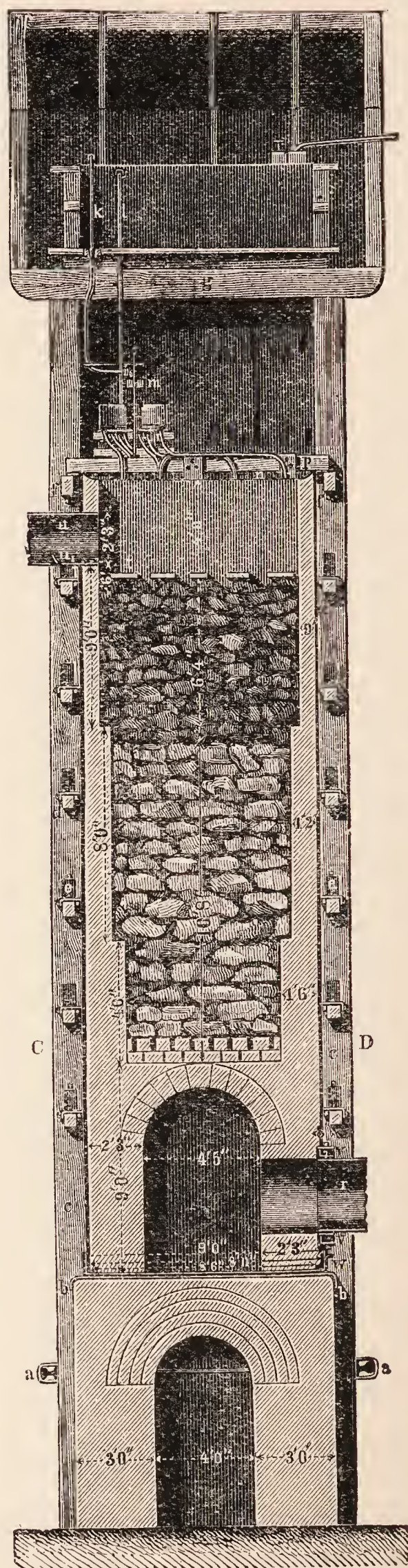


FIG. 8.

600 cub. ft. per ton of sulphur burnt daily is a proportion frequently employed; these figures refer to the total cubic capacity inside the lead,

the actual working space being only about one-half this amount.

Petersen (Chem. Zeit. 1922, 46, 628) suggests decreasing the original cost of constructing the Glover tower by making the internal diameter the same up to the top, and uses thinner walls than usual. The grid supporting the packing is of standard brick. He employs prismatic blocks as packing and Ozag-Petersen's mechanical device for distributing the feed acid.

The gases enter the tower from the burners usually by a cast-iron pipe, and pass upwards through a grating of fireclay slabs or groined arches which carries the packing. Niedenführ recommends the construction of a second arch and grating a little higher up the tower so that the lower portion may be cleaned or replaced without disturbing the main body of the packing (Lüty, Zeitsch. angew. Chem. 1905, 1253). At the top similar arrangements are employed for distributing the acid as in the Gay-Lussac tower. There are two storage tanks on the top, one containing nitrous vitriol and the other chamber acid, and the two streams usually mix in the distributing box before entering the tower. When the additional nitre required for the process is introduced as liquid nitric acid, it is either mixed with the nitrous vitriol in the storage tank or else run into the centre of the top of the tower in a regular stream by means of a glass tube from a Mariotte's bottle, as previously described.

The hot concentrated acid leaves the saucer below by a lip, and is cooled by passing through a leaden trough in which leaden coils or pipes are placed, through which cold water is kept running. Usually Gay-Lussac and Glover towers are built side by side, the latter standing on a higher foundation so that the tops are on the same level. The inspection and control of the two towers is thus much facilitated.

If the Glover tower is fed with nitrous vitriol alone, the latter will not be completely denitrated when it reaches the bottom, but will contain about 0.2 p.c. of N_2O_3 . It is usual, therefore, to mix it with a certain amount of chamber acid of from 110° to 120°Tw . in order to produce a mixture of from 130° to 136°Tw ., from which the nitrous compounds will be completely removed by the hot burner gases by the time it arrives at the bottom of the tower. If more or weaker chamber acid is used, and a mixture is obtained below 130°Tw ., there is danger of loss of nitric oxide from the decomposition of the nitrous vitriol outside the tower; at the same time, instead of obtaining an acid of 150°Tw . or thereabouts, running off at the bottom, the latter may only be 140°Tw ., at which strength it is not nearly so efficient for absorbing the nitrous vapours in the Gay-Lussac tower. It is possible, by keeping the acid in the chambers up to at least 120°Tw ., to pass the whole of the chamber acid made down the Glover tower with the nitrous vitriol, to completely denitrate the latter and to obtain the whole of this acid at 145° – 150°Tw .

The temperature of the burner gas leaving the pyrites kilns will be about 500°C ., and if there is no dust chamber employed the gas will enter the Glover tower at from 400° to 450°C ., and will leave it at between 50° and 80°C . A dust chamber will probably cool the gas another

100°C . before it enters the tower; it will then not be possible to concentrate so much chamber acid in the latter, but perfect denitration can be obtained, the acid running off at the bottom being 140° – 148°Tw . Niedenführ recommends the dividing of the Glover function between two apparatus; after the dust chamber comes a concentrating tower, then a hard lead fan, and then the denitrating tower. Acid of 130°Tw . leaving the second tower is concentrated to 142°Tw . in the first (Lüty, Zeitsch. angew. Chem. 1905, 1253).

Petersen, in order to deal with the large amount of absorbing acid used in working on the intensive system, also recommends the use of two Glover towers, together with two Gay-Lussac towers, the first Glover and the last Gay-Lussac towers working together with acid of 1.7 sp.gr., whilst for the inner towers 1.6–1.65 acid is employed (Zeitsch. angew. Chem. 1907, 1101; Eng. Pat. 27738, 1907; J. Soc. Chem. Ind. 1907, 870; 1908, 981; 1909, 520).

In other cases, where there are several sets of chambers each working with a single Glover tower, some are worked to make strong acid (which need not be denitrated completely) for the Gay-Lussac towers, while the others produce a larger quantity of a weaker acid quite free from nitrous compounds and ready for sale or use.

Where two towers are employed in series the first removes many impurities from the gases, so that the acid concentrated in the second is much purer than that running from the first.

The concentration of the acid in the Glover tower is not due solely to the evaporation of water; it is also very largely due to the production of sulphuric acid in the tower itself, partly from the sulphur trioxide in the burner gas, and partly from oxidation of sulphur dioxide by the nitrous vitriol. Scheurer Kestner found by actual measurement that 17–19 p.c. of the total acid made was produced in the Glover tower, of which about 3.5 p.c. was due to sulphur trioxide in the gases (Bull. Soc. chim. [ii.] 44, 98).

Meyer (Zeitsch. angew. Chem. 1909, 1841) obtained in two cases only 10.8 and 7.3 p.c. of the total make; and Raschig, by estimating the sulphur dioxide in the gases entering and leaving the tower, found that about 14–16 p.c. of the daily production was formed there. Sorcl (Bull. Soc. Ind. Mulhouse, 1889, 240; also J. Soc. Chem. Ind. 1890, 175) explains this formation in the following way: The nitrous vitriol is denitrated in the lower part of the tower, and some of the nitric oxide liberated is oxidised as it ascends, and is reabsorbed by the fresh acid entering at the top and brought down again to be once more denitrated by the sulphur dioxide. In this way a comparatively small amount of nitrogen oxides converts a comparatively large amount of sulphur dioxide into sulphuric acid in the same way as in the chambers subsequently, except that in the tower, the reactions are intensified by the constant subdivision and mixing of the gases, and the contact with a large amount of surface wetted with nitrous vitriol. The heat developed by the intensive reactions in the tower is expended again in evaporating water from the weak entering acid. If the top part of the tower gets too cold, either through the tower being too high or from the large amount of weak acid entering, the denitration will take place in a

comparatively small zone near the top, and less acid formation will take place in the tower. Lunge calculates that with 250 cub. ft. of active Glover tower space per ton of sulphur, and a chamber space of 20 cub. ft. per lb. of sulphur burnt per 24 hours, if $\frac{1}{5}$ of the oxidation takes place in the tower and $\frac{4}{5}$ in the chambers, the denitrating zone of the Glover tower makes 224 times more acid than an equal cube of chamber space (Sulphuric Acid, vol. i. 671).

Metal Traders, Ltd. (Eng. Pats. 213933, 213895, 1923; 187016, 1923; and 149648, 1921) suggest the production of chamber crystals on a large scale by spraying nitrosylsulphuric acid on rollers in a mixing chamber through which gases containing sulphur dioxide and oxygen are forced.

THE CHAMBER PROCESS.

Before starting a set of chambers the saucer should be luted with acid of at least 90°–100°Tw.; if the sides are 'burnt' to the bottom this is not necessary; but water must on no account be used, as it will dissolve the nitrous vapours with the formation of nitric acid which will rapidly attack the lead of the chamber bottom. The dampers are then opened at the end of the system and before the Glover tower, a stream of acid is started running down the latter, the kilns are charged and the hot burner gases are allowed to enter; at the same time three or four times the quantity of nitre required for normal working is charged in the nitre oven or introduced as liquid nitric acid in the Glover tower. As soon as the drips show that sulphuric acid is condensing in the chambers steam is introduced, the quantity admitted being regulated from time to time according to the strength of the drips. Excess of nitre is used until the gas in the last chamber shows a reddish-yellow colour, when the acid feed on the Gay-Lussac tower is started, and as the nitrous vitriol from the latter becomes available for use in the Glover tower, the quantity of fresh nitre is reduced until the minimum required for the regular working of the process is reached.

The strength of the chamber acid.—In England the acid in the first chamber is generally kept at from 120° to 125°Tw., and the steam or water admitted is regulated by the strength of the drips, which usually are 5°–10°Tw. higher than the bottom acid. If the strength exceeds 125°Tw. the quantity of nitrous fumes dissolved in the acid begins to increase very considerably, and the wear and tear of the chamber through corrosion of the lead is notably increased. On the Continent it is more usual to keep the first chamber weaker, from 106° to 110°Tw. The subsequent chambers are all worked a little weaker than the first, the last chamber being usually kept at from 90° to 100°Tw., except in the now very exceptional case where there is no Guy-Lussac tower, when it is reduced to 50°–60°Tw.

The colour of the gases in the chambers requires continuous inspection in order to see if the correct amount of nitre is being used. For this purpose glass windows are let into the sides of the chambers and into the exit pipes from them, the gas being viewed either horizontally through opposite windows or diagonally upwards towards a light in the roof consisting of a

bell-jar placed in a hydraulic lute. Glass bell-jars on a leaden hopper-shaped box are a more convenient method of observing the colour of the chamber gases. The first chamber, owing to the fact that it is full of sulphuric acid mist, will not show any decided colour, but the following chambers should appear distinctly reddish-yellow, the colour gradually deepening till in the last chamber it is dark-red, and even in the exit pipe to the Gay-Lussac it shows a decided colour. The smaller the chamber space employed the deeper this colour will have to be in order to prevent the escape of unoxidised sulphur dioxide, and also nitric oxide with the exit gases from the Gay-Lussac tower. After the latter the gases should show no colour whatever; if they do show a yellowish tint it means that an excess of nitre is being used in the process, or else that the absorbing capacity of the Gay-Lussac tower is insufficient for the nitrous gases present.

Whenever the gases in the last chamber are pale in colour it means that something is wrong; it may be due simply to a shortage of nitre, or it may be caused by too little or too much steam being present; if too little steam is being used the condensing acid will be too strong and will contain much nitrous acid, whilst if too much is being introduced the condensing acid will be weak and will contain nitric acid. Another cause of pale gases is shortage of oxygen due to insufficient draught; analysis of the burner gas or a determination of the percentage of oxygen in the exit gas will at once show whether this is the cause or not. Whatever may be the cause, pale chamber gases mean unoxidised sulphur dioxide and an excess of nitric oxide in the gases entering the Gay-Lussac tower, and as the acid running down the latter will not absorb either of these gases they pass away and are lost. In any case, extra nitre must be introduced at once into the process to replace this loss, and the cause of the disturbance determined and corrected as soon as possible. If too much nitre is being employed the acid condensing in the chambers and in the drips will show the presence of an excessive amount of nitrous acid if tested with ferrous sulphate solution. The bottom acid in the first chamber should give no coloration by this test, and the drip acid only a faint indication. The middle chambers should not give more than a faint indication in the bottom acid and a stronger one in the drips. The last chamber usually gives a decided reaction in the bottom acid and a strong one in the drips. The question of the control of chamber plant is discussed fully by Fairlie (J. Soc. Chem. Ind. 1917, 196, 491). These suggestions are embodied in a patent (U.S. Pats. 1205723/4, 1916). This writer maintains that the oxides of nitrogen are most completely recovered when the proportions of nitric oxide and nitric peroxide in the gases entering the Gay-Lussac tower are exactly those required for the formation of nitrous anhydride. He recommends a sulphur dioxide content of 0.1 to 0.2 p.c. and 5 p.c. or more of oxygen. An acid of 140°Tw. is preferred (see Cory, Chem. Tr. J. i. 1917, 65, 297; 1918, 181, 89; also Met. Chem. Eng. 1921, 25, 186; the last article deals more especially with the engineering aspect of recent developments of the industry).

The regular observation of the temperatures

of the gases in the chambers by means of thermometers with their bulbs several inches inside the walls is very useful in controlling the working of the process. These temperatures depend chiefly on the intensity of the reactions taking place in the chambers; if the outside atmospheric conditions do not vary much, they should be fairly constant when the process is working well. The loss of heat by radiation will vary according to the external temperatures, the force of the wind, &c., more particularly when the chambers are not enclosed in buildings, but the differences between the temperatures of the chambers and the external air should not vary much. The first chamber will be the hottest, and the last the coolest, and different parts of the same chamber will show slight variations, the upper part being a little warmer than the bottom, and the exit cooler than the entrance. There is considerable difference of opinion as to the best temperature for the chamber process. With moderate chamber space the first chamber should not exceed 60° – 70°C ., the later chambers being, of course, cooler, the last showing a reading of 25° – 35°C . In intensive working with only 11 or 12 cub. ft. chamber space the temperatures will be some 20° higher unless means are taken to obtain additional cooling of the gases to that due solely to radiation from the chamber walls. These high temperatures certainly mean additional corrosion, and wear and tear of the lead, and in all probability increased destruction of the available oxides of nitrogen by secondary reactions giving rise to the formation of nitrous oxide and nitrogen. Gaillard (Eng. Pat. 180546, 1921) causes a stream of cold acid to trickle permanently over the whole inner surface of the walls of the lead chambers or towers for the purpose of protecting them from corrosion. Preferably cylindrical or conical chambers are used, cold acid being directed on to the walls by a turbine device. With regard to the lower limit of temperature there is some difference of opinion. Meyer (Zeitsch. angew. Chem. 1901, 1245) states that the temperature for best working is probably above 50°C ., but Lunge is of opinion that the process always works better and with a greater economy of nitre in cold weather than in hot, provided that the temperature does not fall so low that ice is formed in the chambers. On the other hand, since the introduction of water sprays instead of steam, experience seems to show that in very cold weather some steam has to be used, more particularly in the back chambers, in order to obtain the best results.

The pressure of the gases in the different chambers will not be uniform throughout; where only natural draught is employed there is usually a slight outward pressure in the first chamber, in the intermediate chambers the gas is practically in equilibrium with the outside air, while in the last there is a slight suction. These pressures are regulated by means of the dampers between the burners and the chambers, and at the end of the system; where no chimney is employed, and the production of the draught depends chiefly on the upward pressure of the hot gas column between the burners and the Glover tower there is frequently a pressure right through the system, gradually decreasing from first to last.

Where mechanical draught is employed the pressures will depend on the position of the fan. Niefenführ recommends working with a considerable pressure throughout the chambers by placing the fan between two Glover towers and throttling the gas behind the Gay-Lussac tower (Lüty, Zeitsch. angew. Chem. 1905, 1253). But fans are usually placed at the end of the system where they may produce a considerable suction in the chambers. In any case, the draught must be so regulated that the oxygen in the exit gases is not less than 5 p.c., nor greater than 8 p.c. Between these limits opinions differ as to what the excess should be, 6 p.c. being perhaps the most generally accepted figure.

The total quantity of nitre required depends chiefly on the chamber space. Working with pyrites and a chamber space of 24 cub. ft. per lb. of sulphur burnt per 24 hours, this will amount to about 10 p.c. on the sulphur. With less chamber space 15–20 p.c. nitre will be required, whilst for intensive work and a chamber space of 11 or 12 cub. ft. as much as 25 p.c. nitre will probably have to be used. The amount of fresh nitre to be introduced will depend chiefly on the quantity recovered in the nitrous vitriol from the Gay-Lussac tower, and will therefore vary with the efficiency of that apparatus. Generally 3–4 p.c. of fresh nitre has to be used with moderate tower capacity and chamber space; even where the absorbing capacity of the Gay-Lussac tower is very large, the quantity required is never less than 2 p.c., whilst any irregularity in the working of the process may cause a much greater loss of nitre from defective absorption, a correspondingly greater quantity of fresh nitre being required to replace this loss.

Widely different views have been held by different experimenters as to the relative functions of different parts of the same chamber—*i.e.* the lower middle and upper zones, and the portions adjoining the sides and top as compared with the interior.

Mactear (J. Soc. Chem. Ind. 1884, 228), as the result of a series of experiments in which the acid condensing in different parts of the chamber was collected by a number of trays each 1 ft. square, came to the conclusion that most chemical action takes place in the upper part of the chamber, and least near the bottom. Lunge and Naef (J. Soc. Chem. Ind. 1884, 663), on the other hand, deduced from their experiments that the acid formation is greatest near the top, bottom, and sides, and least in the central portion, while Hasenclever concluded that the acid condensed is practically the same per given amount of space in all parts of the interior of a given chamber. There is no doubt that the cooling influence of the external air, together with the surface action of the walls and top, cause a greater condensation of liquid acid along the roof and sides, and Lunge's and Naef's analyses appear to show that there is always more sulphur dioxide in the central part of the chamber than near the outside, pointing to a stronger formation of acid near the chamber walls. They also give a certain amount of support to Abrahams' theory concerning the path taken by the gases within the chambers (Ding. poly. J. 1882, 416). He is of opinion that the cooling action of the walls and top causes the

gas to rise in the centre of the longitudinal section and to descend along the sides of the chamber; so that the gases travel in vertical layers at right angles to the length of the chamber, from front to back, but each single gaseous molecule describes a spiral line, whose axis is parallel to the length of the chamber.

Lunge and Naef have also shown that the conversion of sulphur dioxide into sulphuric acid goes on rapidly in the first half of the first chamber, then slackens very much, but is suddenly revived when the gases pass into the next chamber. This has been confirmed by Schertel (Chem. Ind. 1889, 80), Retter (Zeitsch. angew. Chem. 1891, 4), and others, and is due partly to the better mixing of the gases in passing through the connecting pipe and partly to the cooling and condensing effect of the latter.

The relative amounts of acid formed in a series of chambers have been stated by Hurter (J. Soc. Chem. Ind. 1882, 8) to decrease approximately in geometric progression from the first chamber to the last. Thus with a series of four chambers of equal size, if $\frac{2}{3}$ of the production takes place in the first, $\frac{2}{9}$ will be formed in the second, $\frac{2}{27}$ in the third, and $\frac{2}{81}$ in the fourth. Lunge and Naef have shown that this is only approximately correct.

The examination of the exit gases passing away from the Gay-Lussac tower is a most important part of the control operations requisite for carrying on the process efficiently. Samples may be taken at intervals during each day, or an average sample may be drawn every 24 hours by aspirating a slow stream at a definite rate through a series of absorption bottles containing caustic soda in order to absorb the acid gases. According to the Alkali Works Regulation Act, in England the total quantity of sulphur acids escaping from the exits of sulphuric acid works must not exceed 4 grns. per cub. ft. calculated as sulphur trioxide. This is usually determined by shaking a definite volume of the gas, taken by means of a flexible bellows aspirator, with a solution of hydrogen peroxide and titrating with standard caustic soda solution, using methyl orange as indicator. According to the Alkali Works Inspectors' reports the average acid escapes in England during 1908, 1909, and 1910 were 1.163, 1.162, and 1.178 grains SO_3 per cub. ft. But this test takes no account of the oxides of nitrogen escaping with the gas. Good and reliable methods, based on the reduction of TiCl_3 or 'Devarda' alloy are also employed. Hurter and Lunge (Alkali Makers' Handbook, 98) recommend the following arrangements for estimating the different acids in the exit gases. These agree in the main with those published by the British Alkali Makers' Association in 1878. About 24 cub. ft. of the gases are drawn in 24 hours through four absorption bottles, the first three containing normal caustic soda solution, and the fourth distilled water. The contents are mixed together and divided into three equal parts. One is tested with normal sulphuric acid solution to determine the total acidity. The second is poured into a warm solution of potassium permanganate, strongly acidified with sulphuric acid to oxidise all the nitrogen acids to nitric acid, any considerable excess of permanganate being reduced by sulphur dioxide solution until the colour is a faint pink. It is next mixed in a flask with 25 c.c. of

a solution of ferrous sulphate (containing 100 grms. $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and 100 grms. H_2SO_4 per litre), to which 20–25 c.c. H_2SO_4 has been also added, all air being first expelled by a current of carbon dioxide. The flask is boiled to expel nitric oxide, and the solution is of a light yellow colour, and the unoxidised ferrous sulphate is determined by titrating with $N/2$ permanganate solution. If V be the volume of air aspirated after reduction to 0°C . and 760 mm., x the number of c.c. of normal sulphuric acid used in the first titration, y that of the permanganate used during the second test, and z the quantity of permanganate equivalent to the 25 c.c. iron solution, then the

$$\text{Total acidity } \text{SO}_3 = \frac{\text{Grms. per cubic metre} \cdot 0.12(100-x)}{V}$$

$$\text{Sulphur S} = \frac{0.008(600-6x-z+y)}{V}$$

$$\text{Nitrogen N} = \frac{0.007(z-y)}{V}$$

$$\text{Total acidity } \text{SO}_3 = \frac{\text{Grains per cubic foot} \cdot 1.852(100-x)}{V}$$

$$\text{Sulphur S} = \frac{0.12346(600-6x-z+y)}{V}$$

$$\text{Nitrogen N} = \frac{0.10803(z-y)}{V}$$

Nitric oxide is estimated by passing the gases after leaving the first four bottles through a tube containing 30 c.c. $N/2$ permanganate and 1 c.c. sulphuric acid, sp.gr. 1.25. Excess of standard ferrous sulphate solution is added, and the excess is titrated back by $N/2$ permanganate solution. Then the nitrogen present as—

$$\begin{aligned} \text{NO} &= \frac{0.007 \times A}{3V} \text{ grms. per cubic metre} \\ &= \frac{0.10803 \times A}{3V} \text{ grains per cubic foot} \end{aligned}$$

where A = number of c.c. of $N/2$ permanganate reduced by the NO.

Fig. 9 shows the best form of absorbing

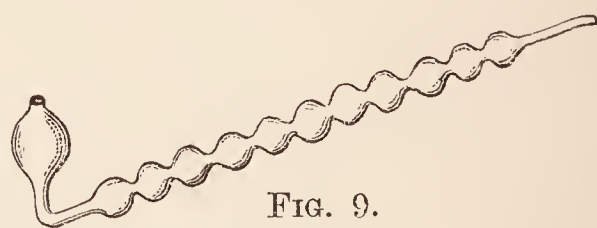


FIG. 9.

apparatus for estimating the nitric oxide according to Lunge.

The oxygen is determined in the residual gas after the acid gases have been all removed.

Carpenter and Linder (J. Soc. Chem. Ind. 1902, 1490) have investigated the methods employed for estimating the acidity of the gases escaping from the chamber process, and find that when soda is used to absorb the acid gases reactions arise with formation of condensation products or sulphazotised bodies whose titre is less than that of the constituents separately, and recommend the use of neutral or alkaline hydrogen peroxide for this purpose.

Proposals for diminishing chamber space.—A number of proposals have been made from time to time for the purpose of increasing the

rapidity of the acid formation in the chambers, and thereby reducing the chamber space necessary for the production of a definite quantity of acid.

Additional surface has been provided by means of lead partitions in the chambers, but these quickly corrode, while partitions of glass soon collapse. Walter and Boenig (Eng. Pat. 14944, 1891) employ double walls of acid-proof material arranged across the whole width of the chambers; the main portion of the gas has to traverse the spaces between these, entering at the bottom and leaving at the top, while the remainder passes through numerous small holes in these partitions.

Niedenführ proposes the division of the chambers into compartments to increase the yield of acid (D. R. P. 241894, 1910); also Rabe (D. R. P. 240474, 1910); Krantz (D. R. P. 283065); Thiele (U.S. Pat. 1267012).

Richter (D. R. P. 15252) aspirates the gases from the lower part of the chamber and introduces them again near the top, and Boult (Eng. Pat. 10757, 1899) brings the gases back from the rear of the apparatus to the front again to obtain a better admixture and circulation.

Rabe (Zeitsch. angew. Chem. 1910, 8, and 1115) suggests methods to facilitate the circulation of gases in rectangular chambers spirally (Abraham's theory) by introducing the gases in the direction of the Abraham currents, by gradually reducing the height of the chamber from front to back or by introducing lead curtains hanging down at intervals a certain distance from the roof, parallel with the ends of the chamber, or the introduction of acid sprays in the direction of the currents. He also criticises Porter's experiments with regard to the movements of the gases in the chambers. But mixing the gases alone is not sufficient, and arrangements for this purpose have not had any great success. Hartmann (Chem. Zeit. 1897, 877) employs a number of shafts 5 or 6 ft. wide from top to bottom of the chamber, luted at the bottom so that a continuous current of cooling air passes up them, and states that he has obtained an increased production of 20 p.c. by this means. Meyer (Zeitsch. angew. Chem. 1900, 74; 1901, 1245) has introduced into the first of his circular chambers a system of cooling pipes, reaching down into the chamber about 8 or 10 ft., and cooled by water which enters the pipes by means of narrower ones reaching nearly to the bottom of the wider ones. By this means he removes 15-20 p.c. of the heat of the reaction, and obtains a corresponding increase in the production. The greatest success, however, in increasing the output of vitriol has been obtained by the employment of mixing and cooling towers between the chambers. Lunge (Zeitsch. angew. Chem. 1899, 385; J. Soc. Chem. Ind. 1889, 774) was the first to introduce these successfully; his plate towers consist of columns of perforated stoneware plates contained in a lead-lined tower into which the gases enter at the bottom and leave at the top. They are fed with a stream of water or dilute sulphuric acid at such a rate that by the vaporisation of water the temperature does not rise above 70° or 80°C. Fig. 10 shows a Lunge tower packed with plates, and Fig. 11 represents the plates in sectional elevation, from which it

will be seen that there is always a thin layer of liquid on each plate, and they are so arranged that the openings in consecutive layers

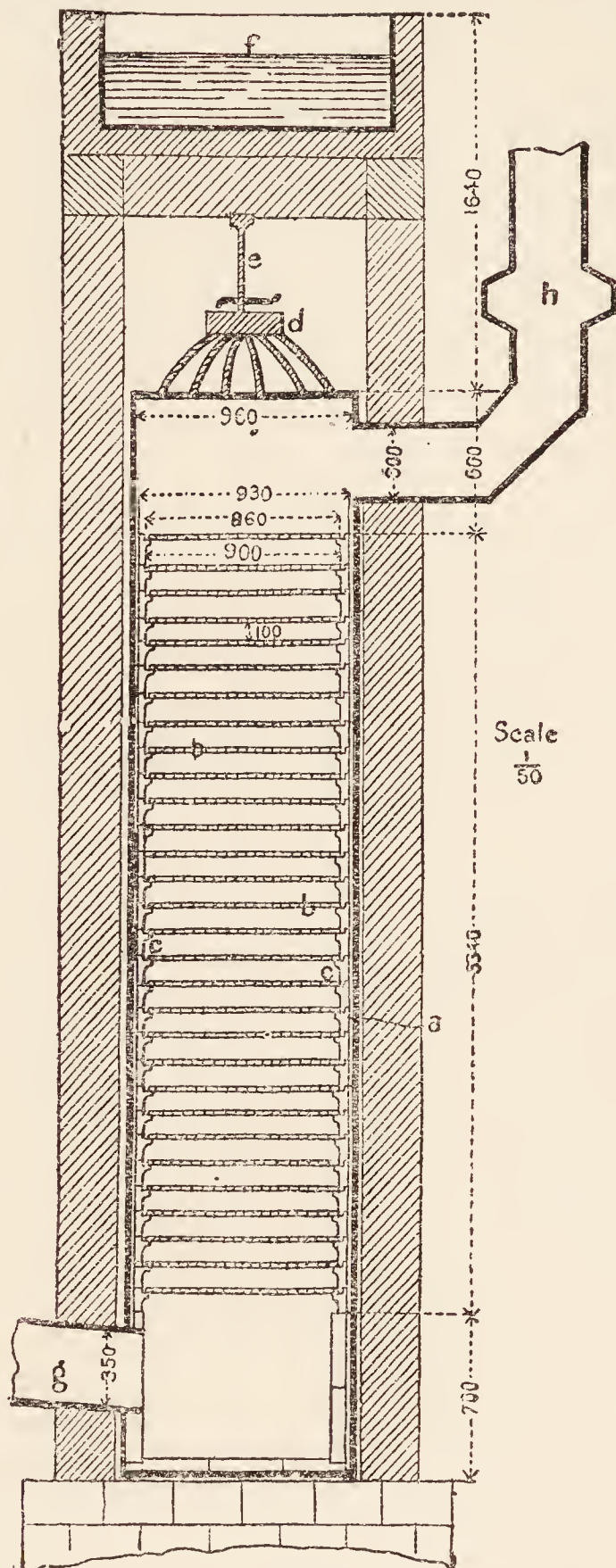


FIG. 10.

are not in the same vertical line. By this means a very intimate contact between the gas and liquid is obtained. According to Lunge, these

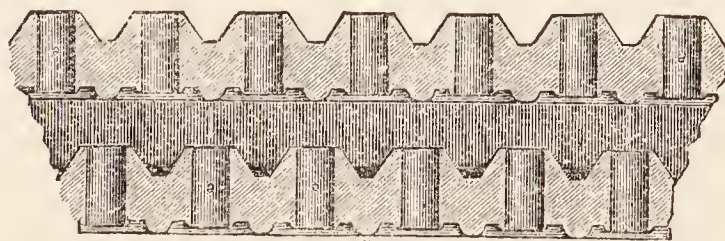


FIG. 11.

towers do from 10 to 20 times as much work as an ordinary coke-packed Gay-Lussac tower of the same cubic capacity, in place of which they are sometimes used. But it is as inter-

mediate towers between the chambers that they are mostly employed. By feeding them with acid above 1.3 sp.gr. the possible formation of nitrous oxide is avoided (Lunge, Ber. 1881, 2200). The heat of reaction in the formation of chamber acid furnishes enough heat to evaporate 100 parts of water at 100°C. during the production of 98 parts H_2SO_4 , a quantity 25 p.c. in excess of the requirements of the process; but most of this excess of heat will be dissipated by radiation from the tower walls (Lunge, Sulphuric Acid, vol. i. 487). Lunge towers have come into considerable use on the Continent; their chief drawback is due to amount of obstruction of draught they cause, but where fans are employed this is easily overcome. Niedenführ (Chem. Zeit. 1896, 31; J. Soc. Chem. Ind. 1896, 541) describes a number of chamber systems where they have been introduced with very satisfactory results. See also Lütty (Zeitsch. angew. Chem. 1897, 484); and Niedenführ (Chem. Zeit. 1897, 20); Lütz and Niedenführ (Zeitsch. angew. Chem. 1902, 242; 1905, 1253).

Other apparatus based on the same principle as the plate towers have been introduced by other inventors. Gilchrist (J. Soc. Chem. Ind. 1894, 1142; 1899, 461) employs pipe columns between the chambers; these are lead towers through which pass from side to side a large number of horizontal pipes cooled by drawing air through them, while the towers are fed with water or acid. Winsloe and Hart (Eng. Pat. 20142, 1901) employ vertical air-cooling pipes set in the connecting trunks between the chambers. Benker (Fr. Pat. 238872) places leaden towers between the chambers 5 ft. wide and 20-25 ft. high, filled with stoneware cylinders; they are fed with nitrous vitriol and steam enters at the bottom with the gases. Guttmann (D. R. P. 91815) recommends hollow balls for packing reaction towers. Hart and Bailey (J. Soc. Chem. Ind. 1903, 473) employ towers between the chambers also provided with vertical tubes through which cooling air passes, and the gases pass down from top to bottom. A novel innovation is suggested by Waggaman, who replaces chambers by a spiral conduit of lead, or in conjunction with chambers (Agric. Bull. 1915, 283, 39; Eng. Pat. 101408, 1916). Petersen introduces an additional tower called the 'chamber-regulator' between the last chamber and the Gay-Lussac towers; nitrous vitriol of 1.6 sp.gr. is continuously circulated through this, and he claims that he obtains a more regular working of the process by this means, and considerable economy in nitre consumption (Chem. Zeit. 1909, 409; Zeitsch. angew. Chem. 1907, 1101; J. Soc. Chem. Ind. 1907, 870; 1908, 981; 1909, 520).

The increase in the size and number of Gay-Lussac and Glover towers, and the introduction of intermediate reaction towers, led Niedenführ (Zeitsch. angew. Chem. 1902, 242) to propose the employment of a system of towers only, without chambers, for the manufacture of sulphuric acid. One type is described as consisting of a number of small chambers around which are grouped the Glover and absorption or reaction towers, the burner gases being passed in succession or simultaneously through the towers before reaching the chambers. Processes have been introduced for this purpose, that of Opl of

Hruschau (Eng. Pat. 20171, 1908; Chem. Ind. 1914, 523; Chem. Tr. J. 1913, 96), and the Griesheim Elektron process (Eng. Pat. 20407, 1909) being perhaps the best known. The burner gases which may have been cooled in a Glover tower are passed through a series of towers in which they are treated with nitric acid. In the first stage, that of oxidation of the sulphur dioxide, it is important that the gas is brought into direct contact with an excess of nitric acid so as to cause almost instantaneous oxidation; for the second stage, that of regeneration of the nitric acid, the apparatus must be of such size that four minutes' contact is maintained. About 15 p.c. of the total tower space is required for the first stage.

Hartmann (Zeitsch. angew. Chem. 1911, 2302) gives details of the Opl process, which has now been at work some years at Hruschau. Six towers are employed like ordinary Glover and Gay-Lussac towers, and are fed by automatic elevators; the pipes leading to towers 3, 4, 5, and 6 are cooled by water; the surplus acid from 2, 3, 4, and 5 is mixed with the whole of that from 6, and finally passed through 1, which it leaves at 1.7 sp.gr. The fan is placed behind 6, and then there is a coke box to remove acid mist so that the exit acidity is only 0.22 grains SO_3 per cub. ft. 18 tons 1.7 acid are produced daily with a reaction space equal

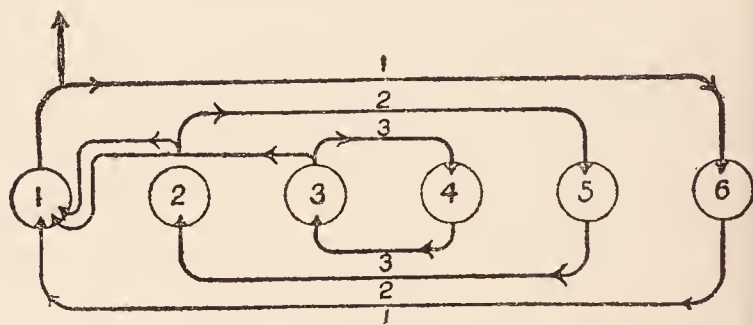


FIG. 12.

to 2 cub. ft. per lb. of sulphur burnt and a nitre consumption equal to 2.25 p.c. on the sulphur. Towers 1, 2, and 3 produce, 20, 30, and 50 p.c. of the acid, the others being simply denitrators.

In the Curtius (Duisberg) tower system (Eng. Pat. 28550, 1913) the gases are introduced at a much lower temperature than is usually employed. Klenke (D. R. P. 284995, 1913) passes the gases in a downward direction through the towers to initiate a vigorous reaction between the nitrous vitriol and gases of a high sulphur dioxide content. Hartmann (D. R. PP. 284636, 1912; 282747, 1915) employs six or more towers. The acid is carried through a series of towers in the form of mist and enters No. 5, which is the main Gay-Lussac. To overcome the tendency of high nitric acid consumption Nos. 1 and 5 and 2 and 6 are paired, so that acid from 5 (highest in nitrous compounds) is conducted to 1, causing the formation of sulphuric acid in the front towers. If the temperature of No. 1 is not sufficient to denitrate, acid is drawn from No. 2 which if fed from No. 6, which has a lower nitrous content than No. 5. Petersen (J. Soc. Chem. Ind. 1912, 487; D. R. P. 258554, 1912) criticises the figures given by Hartmann.

Carmichael and Gillaume (Eng. Pat. 15679, 1913) employ a series of vertical chambers

which are, in turn, left empty and provided with packing. In the Duron (Eng. Pat. 2408, 1913) system each conical tower is fed with previously cooled acid, so that the towers are worked independently of one another. The acid in the concentration towers, of special design, is subjected to the action of superheated gases in a dry state, thus enabling the concentration to be carried to a high degree (*vide* also Burckhardt, Eng. Pat. 29568, 1912; D. R. P. 259576, 1911).

Tungay (Chem. Age, Lond. 1922, 6, 826) describes the Duron Tower system. It consists of six masonry towers, of which one is a small finishing tower, one a Glover tower, two reaction towers, and two Gay-Lussac towers. Of these only the reaction towers need be housed. All

are built slightly conical. The ground space occupied is about 25 p.c. of that necessary for a standard set of chambers.

Littmann and Hoeffling (D. R. PP. 281005, 1914; 281135, 1912) describe reaction towers for intensive working. Piperaut (Mon. Sci. 1920, 10, 49) gives details of a system of towers in series. An exceptional degree of flexibility of output is claimed in the Benker-Millberg system (Ind. chimique, 1921, 8, 93, 222). Further suggestions and useful information on the working of such types of plant will be found in the following articles: Thede, Zeitsch. angew. Chem. 1918; Macnab, Chem. Age, 1922, 6, 872; Chem. Zeit. 1922, 46, 847; Schmiedel and Klenke, Eng. Pat. 149648, 1920.

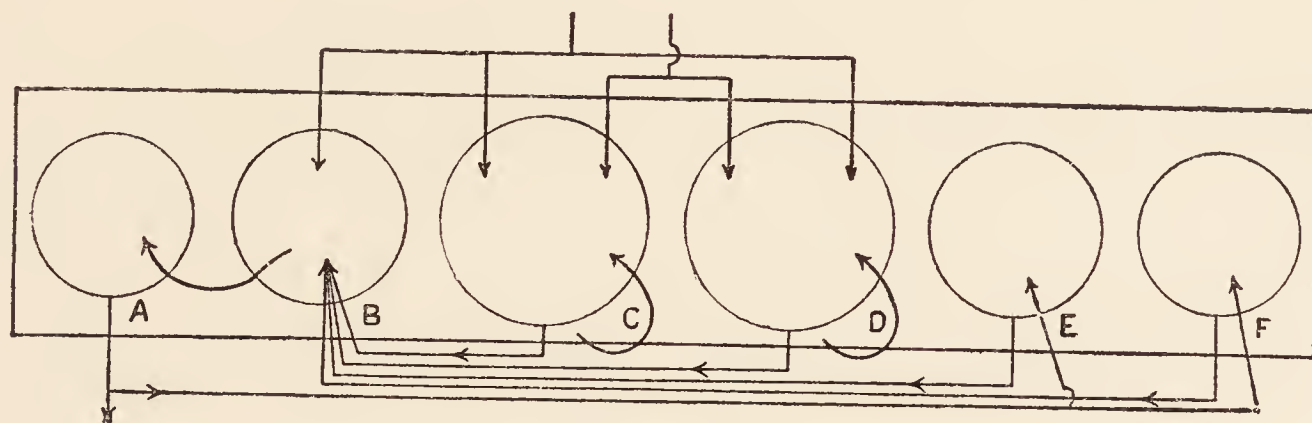


FIG. 13

Schliebs (U.S. Pat. 1151294, 1915) introduces separators between adjacent series of towers and returns a portion of the uncondensed gases to the preceding towers. This writer (Chem. Zeit. 1914, 966, 38) gives the conditions necessary for the production of sulphuric acid in chamber systems which are not fulfilled in the tower systems.

Opl (Chem. Zeit. 1923, 47, 485) describes a modification of the tower system. The gases from the sulphur burners are cooled and forced through a series of iron vessels which are half filled with nitrous sulphuric acid. The denitration takes place in the first vessel, the others acting as nitrators. The residual gases are passed through a tower packed with coke. Petersen (Chem. Zeit. 1923, 47, 227) suggests passing the gases through leaden boxes packed with crushed quartz. The nitrous sulphuric acid flows in the opposite direction. It is difficult to believe that the necessary time of contact between the reacting substances is provided in these suggestions.

Quinan, at the works of the Cape Explosives Co. in South Africa, replaces the chambers by a vertical cylinder fitted with a number of horizontal diaphragms, perforated with a large number of small holes. The sulphurous gases are forced into the compartments of the converter by a fan, which causes a very intimate contact with the descending nitrous vitriol.

McNab (Chem. Age, Lond. 1922, 6, 872) gives the following particulars of the plant erected by Quinan. It consists of a Glover tower, a "converter tower" (U.S. Pat. 1355357), 9 ft. diameter and 10 ft. high, and two Gay-Lussac towers in series. The converter tower consists of a shell containing a number of shelves through which the gases pass so rapidly that the acid is held up on the plates, and runs down

through overflow pipes. The capacity of the plant is 2 tons per hour. The erection costs are less than for an ordinary chamber plant, but power for acid pumping and fans are greater.

Another method of securing the intimate contact between the reacting gases and liquid acid is effected by Schmiedel (Eng. Pat. 187016, 1922), who employs a horizontal rectangular 'splash box' of lead, in which rotating drums dipping into the acid produce a film through which the gases are forced. The series of boxes are followed by absorption towers. An installation of this type has been working for two years in connection with the utilisation of the gases from the copper matte converters at Ausserfelden in Austria (*see* Parrish, Eng. Pat. 156328; also Chem. Age, Lond. 1924, 316).

Other patents of Schmiedel are: Eng. Pats. 149647/8, and 184966, 1921.

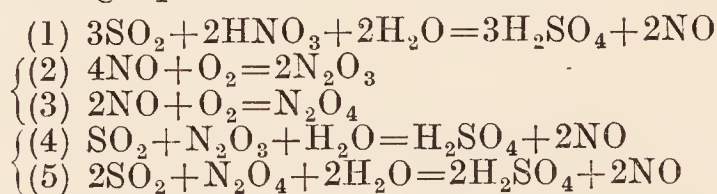
Petersen (Chem. Zeit. 1923, 47, 227) comments on the method of sulphuric acid manufacture in which neither lead chambers nor towers are used. In an ordinary lead chamber plant, with intensive working, 200 tons of lead are necessary to produce 35 tons of 50 acid per 24 hours. This lead, without erection costs, constitutes about 40 p.c. of the total cost of the plant, exclusive of the burners. The Opl tower system and the Schmiedel-Klencke system depend on the ability of 55 acid to be denitrated easily, or to take up oxides of nitrogen readily. The extensive mechanical development of Schmiedel and Klencke costs more in upkeep and operation than is saved in interest and repairs of the lead chambers.

Various forms of apparatus to bring about the necessary intimate contact between the sulphur dioxide and this acid were described by Petersen in his patent of 1905.

THEORY OF THE CHAMBER PROCESS.

A large number of different views as to the nature of the normal chemical changes taking place in the vitriol chamber (as well as of those occurring under abnormal conditions) have been from time to time put forth by different observers. The basis on which all these views are founded is the fact that the higher oxides of nitrogen in one way or another bring about the oxidation of the sulphur dioxide in presence of water or steam to sulphuric acid, being reduced to lower oxides which take up oxygen again and then continue the cycle of changes as before.

The theories of Weber and Berzelius were very simple, and may be represented by the following equations:—

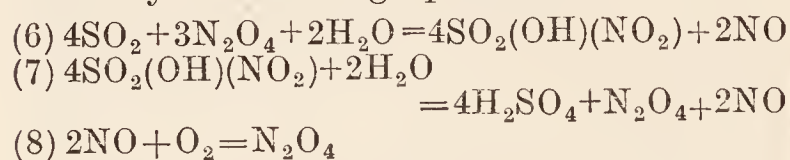


Weber believed that equations (2) and (4) represented the chief reactions occurring, N_2O_3 or nitrous acid being the active agent, whilst Berzelius was of opinion that N_2O_4 also played an active part in the process.

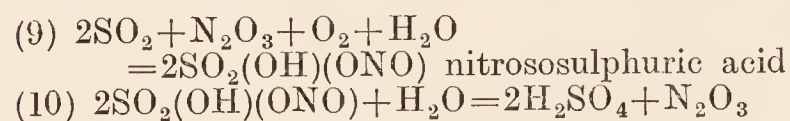
The steam, oxides of nitrogen, and sulphur dioxide react, producing a fine mist of dilute sulphuric acid.

If sufficient water be not present crystals separate of the composition $\text{SO}_2(\text{OH})(\text{NO}_2)$, a substance known as *nitrosylsulphuric acid*, *nitrososulphuric acid*, *nitrosulphonic acid*, or *chamber crystals*; but these are decomposed again into sulphuric acid and nitrous acid by excess of water or steam.

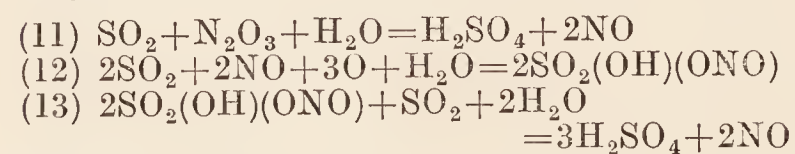
Davy and Winkler were of opinion that this substance was a temporary intermediate product in the process, and their views were represented by the following equations:—



Lunge's earlier ideas were similar only that he represented N_2O_3 as the active substance, and not NO , and his views are thus represented—



By N_2O_3 here is meant the equivalent mixture of NO and NO_2 . Lunge believed that this represented the chief cycle of reactions in the process, but stated that they must be modified in the first part of the chambers where there is present a large excess of NO above the proportion $\text{NO} + \text{NO}_2$. Here the following reactions may take place:—

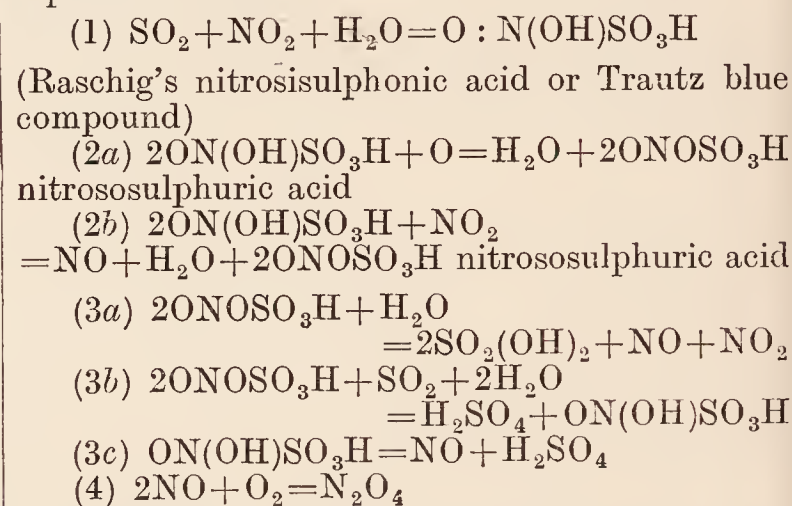


The last reaction represents what takes place in the Glover tower, the conditions being identical in both cases.

During the last few years a number of different views have been put forward by Lunge, Raschig, Divers, Wentzki, and others, of the

reactions taking place in the chambers, which differ from each other chiefly in conceptions as to the nature of the intermediate substance or substances which are formed by the interaction of sulphur dioxide, the oxides of nitrogen and water, and which afterwards split up, yielding sulphuric acid and a lower oxide of nitrogen.

Lunge's latest ideas are given in an article published by him in conjunction with Berl (Zeitsch. angew. Chem. 1906, 19, 807-819, 857-869, 881-894). The following equations represent these:—



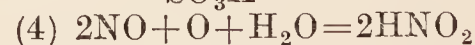
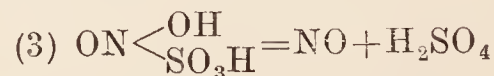
Equations (1), (2a), and (3a) represent the chief cycle of reactions which takes place, whilst (1), (2b), (3b), (3c), and (4) most likely represent the reactions occurring in the first chamber where there is an excess of sulphur dioxide and much nitric oxide.

Raschig's theory of the nature of the changes by which sulphur dioxide passes into sulphuric acid was first published in 1887 (Annalen, 1887, 241, 161), but it has been several times considerably modified since then. His latest ideas were published in Zeitsch. angew. Chem. 1907, 20, 694, and further elaborated and explained in a paper read before the Society of Chemical Industry in 1911 (J. Soc. Chem. Ind. 1911, 4, 166).

He represents the following reactions as taking place:—

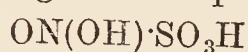
(1) $\text{HNO}_2 + \text{SO}_2 = \text{ONSO}_3\text{H}$, *nitrososulphonic acid*, a purely hypothetical substance which has not been isolated.

(2) $\text{ONSO}_3\text{H} + \text{HNO}_2 = \text{ON} \begin{smallmatrix} \text{OH} \\ \text{SO}_3\text{H} \end{smallmatrix} + \text{NO}$ *nitrosylsulphonic acid*, which he believes to be identical with the blue compound formed when excess of sulphur dioxide is passed through a solution of nitrosulphonic acid $\text{O}_2\text{N} \cdot \text{SO}_3\text{H}$ in concentrated sulphuric acid, and to be the cause also of the purple colour of Gay-Lussac acid when sulphur dioxide is in excess in the exit gases from the chambers—



Raschig (Schwefel und Stickstoffstudien, 1924, 1; Chem. Zentr. 1924, 95, ii. 16) suggests a ring structure for the stable SO_2 complex in sulphurous acid and its salts, sodium sulphite and sodium bisulphite having respectively the formulæ $\text{Na}(\text{O} :)\text{SO}_2 \cdot \text{Na}$ and $\text{H} \cdot \text{SO}_2 \cdot \text{ONa}$. These formulæ explain why sodium sulphite does not react with nitrites at the ordinary temperature, whereas sodium bisulphite reacts readily, steric hindrance due to the central position of the sulphur atom in sodium sulphite and sodium

nitrite with the formation of sodium nitrilo-sulphonate, $N(SO_3Na)_3$, is rendered possible at high temperatures by hydrolysis of the sodium sulphite into sodium bisulphite and sodium hydroxide. Equimolecular proportions of nitrous acid and sulphurous acid interact with the formation of nitrososulphonic acid in accordance with the equation $HNO_2 + SO_2 = ONSO_3H$, and sulphuric acid can only be detected after one minute, whilst compounds containing 2 and 3 sulphonyl groups are only formed when there is considerable excess (5 or 20 times respectively) of sulphurous acid. In the presence of non-reacting acids, nitrososulphonic acid combines less readily with sulphur dioxide than in their absence, but shows a greater tendency to react with one mol. of nitrous acid, liberating nitric oxide and forming nitrosisulphonic acid



This acid, which is somewhat stable in cold concentrated sulphuric acid solution, is of a blue colour which deepens on the addition of copper salts, and changes to bordeaux-red on the addition of ferrous salts; it is also produced by the reduction of nitrosulphonic acid in sulphuric acid solution by copper or mercury and in the nitrometer, and decomposes rapidly on heating into nitric oxide and sulphuric acid (J. Soc. Chem. Ind. 1924, 43, B, 709).

A review of Lunge's theory of the chamber process is given by Irwin (Chem. Age, Lond. 1922, 7, 938).

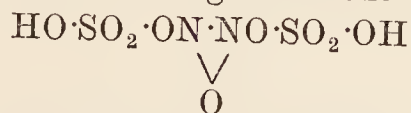
Divers (J. Soc. Chem. Ind. 1911, 10, 594) has again modified Raschig's theory. He believes that this transitory substance, identical with the compound which gives the colour to purple acid, has the composition $H_2N_2SO_6$, which he calls *nitroxysulphuric acid*, and that it is the only intermediate substance formed in the reaction.

His views are represented as follows:—

- (1) $2HNO_2 + SO_2 = H_2N_2SO_6$
- (2) $H_2N_2SO_6 = 2NO + H_2SO_4$
- (3) $2NO + O + H_2O = 2HNO_2$

Wentzki (Zeitsch. angew. Chem. 1910, 1707; 1911, 392; 1914, 112, 218) criticises Raschig's and Lunge and Berl's views, and is of opinion that neither nitrosylsulphuric acid (chamber crystals) nor the blue compound can exist in the chamber when excess of sulphur dioxide is present, and that sulphuric acid may be produced from sulphur dioxide, nitrous gases, and water without the formation of any intermediate compounds, as in Weber and Berzelius' early theory.

The blue compound he calls *nitrosylous sulphuric acid*, and he gives it the constitution



Jurisch (Chem. Zeit. 1910, 1065) and Manchot (Zeitsch. angew. Chem. 1910, 2113, and 1912, 1055) criticise Raschig's formulæ for the composition of chamber crystals and purple acid.

Reynolds and Taylor (J. Soc. Chem. Ind. 1912, 367) also unfavourably criticise Raschig's conclusions, and support the early simpler theory.

Whichever of these various views of the nature of the chemical reactions taking place be regarded as most probable, and it is impossible to enter here into the details of the experimental evidence in favour of each, no doubt whatever

can be entertained that none of them accounts for the whole of the chamber phenomena; for even with the best-designed and most perfectly working system of nitre recovery, there is always a loss to be accounted for, which amounts to at least 2 parts of nitre per 100 parts sulphur burned as pyrites, the average loss being 3–4 parts.

Considerable difference of opinion exists as to what proportion of this is lost by incomplete absorption in the Gay-Lussac tower either as NO or N_2O_3 and N_2O_4 ; but this cannot account for the whole of the loss; there remains a very considerable proportion which can only be put down to other chemical reactions taking place in the chambers and causing reduction of the higher oxides of nitrogen to nitrous oxide, nitrogen, or other nitrogenous compounds, or even to ammonia.

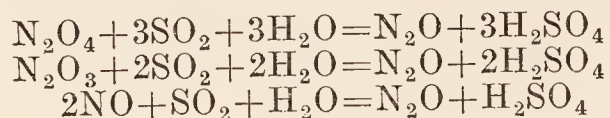
The loss through incomplete absorption may be called mechanical loss. Figures have been obtained by Lunge, Davis, Jackson, Mactear, and others, indicating amounts of escape equivalent to from 1 to 1.75 parts of nitre per 100 of sulphur burnt as usual proportions; whilst Hurter, Eschellmann, and others consider 0.25–0.5 as more nearly the amount thus lost on the average with efficient plant in good working order. From the results obtained in a variety of works Hurter concluded (Chem. News, 39, 170) that the total loss of nitre from mechanical sources (*i.e.* defective absorption, formation of nitric oxide, leakages, and solution in chamber acid jointly) does not amount to as much as 25 p.c. of the nitre charged, at least 75 p.c. being lost by chemical secondary changes. E. K. Muspratt states (J. Soc. Chem. Ind. 1884, 137) that the result of experiments made in ten different works by a committee of the Alkali Makers' Association was that the total loss by non-absorption in the Gay-Lussac tower averaged close to 20 p.c. of the nitre used, that being 4 parts per 100 of sulphur burnt. Eschellmann found (*ibid.* 1884, 134) that out of 2.75 parts of nitre per 100 of sulphur burnt, 0.33 part (12 p.c.) was accounted for by non-absorption in the Gay-Lussac tower of soluble nitrogen oxides, and 0.19 part more (7 p.c.) by the formation of nitric oxide, representing a total of 0.52 part (19 p.c.) of loss due to available nitrogen oxides of all kinds; to which 0.08 part (3 p.c.) must be added for leakages and retention in the acid; thus leaving 2.15 parts (78 p.c.) not accounted for by mechanical losses, but destroyed by secondary chemical changes.

On the other hand, Lunge, Benker, Sorel, and others are of opinion that the greater proportion of the loss is due to incomplete absorption, owing to the fact that the coefficient of solubility of N_2O_3 in sulphuric acid is immensely reduced by its enormous dilution in the exit gases with oxygen and nitrogen, and that, therefore, its complete absorption is an impossibility. Sorel has attempted to prove in a special instance (Zeitsch. angew. Chem. 1889, 279) that the exit gases were bound to carry away N_2O_3 equivalent to 3.09 parts nitre per 100 sulphur burnt, and Lunge states (Sulphuric Acid and Alkali, vol. i. pt. ii. 954) that it is extremely difficult by ordinary analytical methods to estimate the quantities of N_2O_3 or N_2O_4 passing away into the exit gases, whilst the escaping NO is still more difficult to determine accurately.

Considerable support has been given to the view that the mechanical losses constitute the greater proportion of the total loss by some experiments made by Inglis at Silvertown (*J. Soc. Chem. Ind.* 1907, 668). He condensed a number of samples of the exit gases by means of liquid air, and afterwards separated the various constituents by fractionation. He was able to account for between 50 and 60 p.c. of the loss as due to incomplete absorption, partly as N_2O_3 , and partly as NO , the total loss being 2.58 parts nitre per 100 parts of sulphur burnt. However, even his figures leave some 40 p.c. loss of nitre to be accounted for as chemical losses. At one time the Glover tower was blamed, it being supposed that considerable reduction of the nitrous gases to nitrous oxide by the excess of sulphur dioxide present took place there, but this has been practically disproved by the fact that quite as good results are obtained when nitric acid is run through the tower as when it is introduced into the chambers direct; whilst the quantity of available nitrogen oxides contained in the gases passing out of the tower can be shown analytically to correspond practically with the quantity contained in the nitrous vitriol run into the tower. It has also been suggested that there is some loss in the Gay-Lussac tower owing to the reducing action of arsenious oxide in the acid, or to the coke packing, but this is again disproved by the fact that with brimstone acid, where there is no arsenic present, the same loss occurs, and also with towers packed with other materials than coke.

Hence any material chemical loss must be confined to the chambers themselves in virtue of secondary reactions.

It has long been known from the experiments of Pelouze and Weber, more recently repeated and amplified by Lunge, that in contact with water or highly dilute sulphuric acid, higher oxides of nitrogen are slowly acted on by sulphur dioxide, with formation of nitrous oxide, thus—



but in contact with stronger acid these actions take place either not at all or only extremely slowly. Consequently this action is only likely to take place where water or aqueous vapour is in excess, and that will be only in the immediate vicinity of the entering steam. That this reduction does take place is now generally admitted, but to what extent and what proportion of the loss is due to it there is considerable difference of opinion. Inglis, in the experiments alluded to above, could only account for about 10 p.c. of the loss as nitrous oxide in the exit gases, but Hempel and Heymann (*Zeitsch. Elektrochem.* 1906, 600) state that they obtained nitrous oxide in the exit gases from several works varying from 0.063 to 0.25 p.c. where 0.1 p.c. nitrous oxide would be equivalent to a loss of 4.3 parts nitre per 100 parts sulphur burnt.

A further reduction to nitrogen may also take place, but no proof of this is possible, whilst Raschig is of opinion that even ammonia may be formed by secondary reactions, but, in general, this would probably at once react with nitrous acid to give nitrogen and water. In some cases, however, where the chamber acid

contains free sulphurous acid he has found traces of ammonia present in the acid (*J. Soc. Chem. Ind.* 1911, 172). Further views are given by Briner and Kühne (*Compt. Rend.* 157, 443, 1913).

Briner and Rossignol (*Helv. Chim. Acta*, 1923, 6, 647), using known mixtures of SO_2 , NO_2 , H_2O , O , and N , have studied the formation of sulphuric acid by the chamber process. They conclude that the amount of acid formed in unit time is proportional to the square of the gross gas concentration, or the square of the absolute pressure. The accelerating effect on the reaction rate of the surfaces of the containing vessels is emphasized.

An elaborate study of the physical and chemical reactions of the lead chamber process has been made by Forrer (*Bull. Soc. chim. Belg.* 1922, 31, 254).

PURIFICATION.

All pyrites acid contains more or less iron, arsenic, and other substances derived from the ore employed, the contamination being considerably greater in the case of acid from the Glover tower than in that from the chambers. For many purposes these impurities are of no great importance, but for others, a purer acid is required, and various processes have been devised for removing these impurities, more especially from the chamber acid. Suggestions for purifying burner gases from arsenic and iron have been published (*Chem. Abstr.* 1914, 1959).

The chief impurities are arsenic, antimony, selenium, lead, iron, nitrous acid, and organic matter. The lead is almost entirely precipitated on diluting the acid; the iron largely separates during concentration, especially in the platinum still, organic substances being oxidised at the same time.

The most serious impurity is arsenic, which is nearly always accompanied by antimony and selenium, and nitrous acid.

Arsenic.—Pyrites chamber acid made from Spanish pyrites usually contains from 0.05 to 0.2 p.c. arsenic, as arsenious oxide, whilst the Glover tower acid may contain as much as 1 p.c. or more, partly as As_4O_6 and partly as As_2O_5 .

There are two methods employed on a considerable scale for the removal of arsenic. The first is by precipitation as arsenic sulphide by sulphuretted hydrogen. The latter is generated usually from ferrous sulphide by the action of weak sulphuric acid in wooden vessels lined with lead, and the gas passes into a tower packed with rows of horizontal wooden bars of triangular section covered with lead. A stream of chamber acid, from 100° to 110°Tw., is fed into the tower by a distributing arrangement at the top. Usually several generators are employed, so that, by charging them alternately a fairly uniform current of gas can be obtained, and the arsenic should be completely precipitated by the time the acid arrives at the bottom of the tower, from which it is run or blown into settlers. From these it runs on to sand filters, which it leaves practically free from arsenic; it should not contain more than 1 part in 500,000 parts acid. When alkali waste is available, the sulphuretted hydrogen is frequently obtained from that source. Nitrous acid, antimony, selenium, lead, &c., are removed also by this method, and except for the presence of a small

quantity of iron the acid is practically as pure as brimstone acid. The towers may be effectively replaced by cast-iron washers (Davis, Met. and Chem. Eng. 1914, 354; Eng. Pat. 2113, 1909), in which intimate contact between the acid and the hydrogen sulphide is ensured by spraying the former by means of revolving blades (Fig. 14). Acid of considerably higher strength than 110° – 120° Tw. can be treated where a cheap and abundant supply of hydrogen sulphide is available. The gas is pumped into the acid under pressure (Cory, Chem. Tr. J. 1918, 62, 89; J. Soc. Chem. Ind. 1918, 37, 122). By agitating the acid, after treatment with hydrogen sulphide, with a liquid hydrocarbon, the scum so formed is readily removed by scrapers. The hydrocarbon may be recovered and returned to the plant by washing the scum with water (Warcing and the United Alkali Co., Eng. Pat. 126714, 1919).

The second method employed on a manufacturing scale for the removal of arsenic depends on the conversion of the arsenic into trichloride by treatment with hydrochloric acid, and the removal of the latter by heat. Common salt and barium chloride have been tried instead of

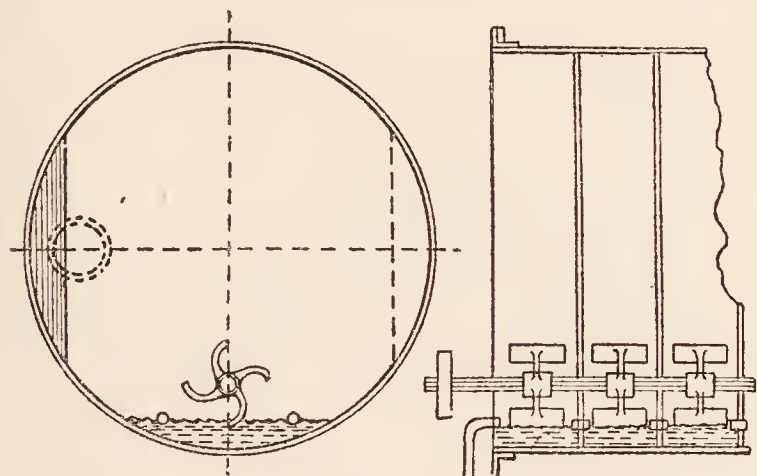


FIG. 14.

hydrogen chloride, but they have not been successfully used on a practical scale. It is necessary that any arsenic oxide in the acid should first be reduced to arsenious oxide. The United Alkali Co. have patented a process for treating Glover tower acid with hydrogen chloride at 100° , and removing the liquid arsenic chloride which separates by blowing air through it; any arsenic oxide present is reduced by treatment with charcoal or sulphur (Eng. Pats. 7916, 16929, 16930, 1905; 23139, 1906).

The arsenic chloride may also be removed by treatment of the acid with certain mineral oils or oil from lignite tar (Hasenbach, U.S. Pat. 836034, 1906; and Verein. Chem. Fabrik. Mannheim, Fr. Pat. 368452, 1906).

Nitrous compounds or nitric acid are removed from sulphuric acid by heating with a small quantity of ammonium sulphate, whereby ammonium nitrite or nitrate is formed and at once decomposed with evolution of nitrogen or nitrous oxide. This is especially necessary where the acid is to be concentrated in platinum vessels in order to prevent serious corrosion of that metal.

Non-volatile impurities can only be completely removed by distillation of the concentrated acid. This may be carried out in glass retorts, and is a troublesome operation owing to the liability of the retorts to crack;

as the impurities accumulate in the retort they cause serious bumping. Scraps of platinum or quartz, &c., are frequently introduced to prevent this, or a slow current of air is passed through the boiling acid. Where a very high grade of purity is required, as is the case in the acid used as a reagent, distillation in platinum stills is usually employed.

Iron is practically insoluble in 100 p.c. sulphuric acid, so that by bringing the acid up to that strength by mixing with fuming acid, and allowing to stand for some months, practically all the iron separates out.

CONCENTRATION.

Before the invention of the Glover tower chamber acid of 110° – 120° Tw. was always evaporated down in leaden pans until the sp.gr. rose to about 140° – 145° Tw., when the action on the lead became too great for further concentration to be thus possible. Such pans are still in use to a considerable extent; when contamination by fuel gases is immaterial they are heated by passing the flame over the liquid (top-firing); in which case the concentration may be carried to 150° Tw.; a certain amount of acid is always carried away in the current of fire gases when this method is employed. It escapes as a vesicular mist, which can only be condensed by filtration through fine granular material.

In other cases the pans are heated from below, the lead being protected from direct contact with the flame by iron plates. Waste heat from various sources is often used for heating the pans; sometimes they are mounted on the top of the kilns or on the burner gas flue, so as to partly utilise the heat of combustion of the sulphur burnt. Glover at one time employed a large platinum dish, placed inside the gas flue from his brimstone burner for concentrating chamber acid up to 140° Tw. High pressure steam passing through lead coils has also been used instead of directly fired pans.

For the further concentration up to from 93 to 98 p.c. H_2SO_4 , glass or platinum stills were at one time chiefly used, but the great losses through breakages of the former and the great rise in the price of the latter, have led to their being displaced by other materials and methods of concentration, of which the Kessler and Gaillard processes have been most successful.

Negrier (J. Soc. Chem. Ind. 1891, 46) patented an arrangement (Veitch, *ibid.* 1889, 983), using porcelain dishes instead of glass retorts, the lip of one dish projecting over the next below in the series. Two series of dishes are mounted side by side, fed from the same cistern, each dish resting on asbestos tissue and surrounded by sand up to the level of the upper rim; the supporting shelves are of iron.

Benker has improved the Negrier system by enclosing the porcelain dishes in a chamber of volvic lava. The flue gases are kept separate from the acid vapours, which are condensed in a lead-lined box filled with granular stoneware or silica. The dishes are covered with a thin layer of asbestos and silicate of soda cement, and the acid may be concentrated up to 97–98 p.c. H_2SO_4 (Zeitsch. angew. Chem. 1903, 1150). The porcelain dishes have, with advantage, been replaced latterly by vessels made of fused

silica or metillure. The usual arrangement, known as the Cascade System, consists of a series of basins placed in terraces and heated from below. The basins may be of silica or acid-resisting alloy ('Tautiron,' 'Duriron,' 'Ironac,' 'Narki'). The basins may be associated with leaden pans, for the preliminary heating, and iron troughs for the lower end. The use of cascade systems is rapidly giving place to other methods (Met. & Chem. Eng. 1915, 7; Eng. Pats. 13642, 1914; 1495, 16001, 1915; 101642, 104034, 1916). The concentration of sulphuric acid by hot gases has been carried to a high degree of efficiency. Methods of utilising reduced pressures to facilitate the concentration have also been patented (D. R. P. 242373, 1910; Eng. Pat. 10386, 1915).

Platinum stills, formerly very largely used, have been considerably modified since their first introduction. Long narrow and shallow stills, with the bottom corrugated to increase the heating surface, are preferable. The vapours are condensed in a water-cooled platinum tube. The loss of platinum by corrosion has been variously estimated (Chem. Zeit. Rep. 15, 36; J. Soc. Chem. Ind. 1891, 460; 1892, 522). Conroy has investigated the influence of various impurities in the acid, and the effect also of temperature on the corrosion of platinum vessels. Heraeus (Eng. Pat. 2499, 1891) has patented a process for covering the surface of the platinum vessels with a compact adhesive layer of gold, the diminution of corrosion being very considerable.

Cast-iron vessels are in use for the production of acid of high strength up to 98 p.c. H_2SO_4 . The acid may be brought up to 93 or 94 p.c. and then to the highest strength in cast iron. There is a certain amount of action on the iron even at these strengths, but the contamination of the acid is not serious, as the sulphate mostly separates as an insoluble precipitate as the acid becomes fully concentrated. Sometimes cast-iron pans are employed with leaden covers, as in Faure and Kessler's system. If iron covers are used they must be kept hot so that no weak acid can condense on them. Cast-iron vessels seldom last more than 4-8 months. Weak acid can be concentrated in a deep cast-iron pan by running it on the surface of the heated acid, which is not allowed to drop below 90-93 p.c. H_2SO_4 , the strong acid being at the same time withdrawn from the bottom. Cast-iron vessels are used for concentrating waste acids and impure Glover tower acid where the separation of impurities would render concentration in glass or platinum apparatus practically impossible. Hartmann (Chem. Zeit. 1899, 147) describes their use for concentrating waste acid from nitrating processes. Cast-iron dishes made of the so-called 'neutral iron' by the A. G. für Bergbau und Eisen-Hüttenbetrieb at Kattowitz, Silesia, are now used by Hartmann and Benker for concentrating on the Benker system, and the acid comes out water white and not distinguishable from acid concentrated in platinum (Lunge's Sulphuric Acid, vol. i. 1176).

The Kessler process for the concentration of sulphuric acid by means of hot gases (Eng. Pats. 19215, 1891; 26169, 1898; 21376, 1900) has proved one of the most successful of the processes for this purpose. The hot gases from

a producer charged with coke are drawn by means of a steam exhauster over the surface of the acid in a large shallow trough of volvic lava with a thick lead jacket, called the *saturex*, and then through a column, the *recuperator*, the lower section of which is of lava and the upper one of lead, where they come into intimate contact with a descending stream of weak acid which retains most of the acid vapours, but allows the steam to pass on to a large lead-lined condenser filled with coke crushed to the size of rice grains. This filters out the remainder of the acid vapour, and allows only aqueous vapour to escape. Fig. 15 gives a sectional elevation of the *saturex* and recuperator. The steam exhauster is placed in the connection between the recuperator and the condenser, and the steam and acid vapours pass downwards through the latter. The use of compressed air in the place of steam reduces the amount of weak acid produced, but both steam or air jets are replaced by fans with advantage.

The concentrated acid is not so pure as that obtained in Benker's process, and seldom exceeds 95-96 p.c. H_2SO_4 . A much larger condenser or

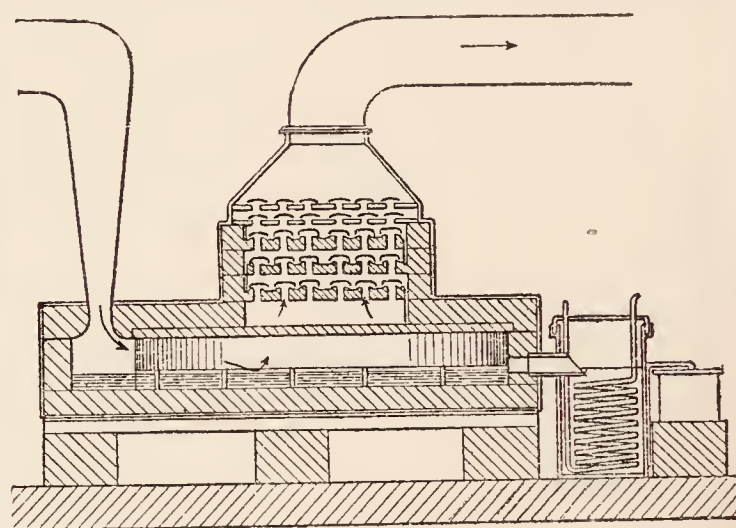


FIG. 15.

filter is also required, owing to the dilution of the acid vapours with the fuel gases. The *saturex* may be built up of a series of troughs and of considerably greater length than was formerly customary. Another form of concentrator which combines the advantages of other types and which is likely to prove an efficient form of apparatus is the 'Gilchrist' (Oliver, Eng. Pat. 105993, 1917). Hot gases, preferably from oil burners, pass over the surface of the acid, which is agitated by air, and then upwards through a tower, down which acid is flowing. A series of interesting details of a tower concentrator plant, for the production of 93-97 p.c. sulphuric acid, is given by Armstrong (J. Ind. Eng. Chem. 1917, 386; U.S. Pats. 1211594, 1232109, 1917; Monit. Scient. 1917, 265). Gilchrist (Chem. Age, N. York, 1922, 30, 257) discusses cascade, cascade-tower, and tower systems of sulphuric acid concentration. The surface evaporation-tower and hot-air submergence systems are fully described, and a drawing of the type patented by Gilchrist and Hechenbleikner is shown. The article is a good review of the whole process of sulphuric acid concentration. Calculations of the heat required in concentration are given by Sutton (Chem. Age, 5, 178). Gilchrist (Chem. Met. Eng. 1922, 26, 1159) compares the various

systems of concentration and supplies information as to costs.

Cerutti, however, has pointed out that Sutton has omitted several sources of error, such as the assumption that the heat of vaporisation for water is constant over the whole range, the use of the lower instead of the average specific heat over a given temperature range, and the assumption of a 20 p.c. radiation loss for a Gaillard plant, which seems low in view of a radiation loss of 75 p.c. actually obtained on a modern cascade concentrator (Chem. Age, Lond. 1921, 5, 759).

In the Gaillard process (Eng. Pat. 12538, 1906; Chem. Zeit. 1910, 173; Hutin. Rev. Chim. Ind. 27, 49) the concentration is also brought about by means of hot gases. The dilute acid is sprayed by means of atomisers into the top of a cylindrical tower of volvic lava, in which it meets the hot products of combustion from a generator fed with coke. The hot gases enter near the bottom and leave at the top, from which they pass to a number of leaden boxes containing fine coke to remove the acid-vapours. The acid arrives at the bottom of the tower in a concentrated state. This process has proved particularly useful for concentrating very impure chamber acid, and also for waste acids from petroleum refining. Stolzenwald (Zeitsch. angew. Chem. 1910, 175) and Duron (*ibid.* 1910, 2307) compare concentration up to 98 p.c. H_2SO_4 in Gaillard and Kessler plants with concentration in cast-iron boilers and pans (Chim. et Ind. 1921, 5, 143).

Zeisberg (Chem. Met. Eng. 1922, 27, 22) reviewed the literature on the specific heat, boiling-point, and heat of dilution of various concentrations of sulphuric acid. The composition of vapours in contact with boiling sulphuric acid solutions is also given. Graphs are drawn which give the heat necessary to raise one pound of acid of various strengths from various temperatures to the boiling-point, and the heat necessary to concentrate one pound of acid of any strength at the boiling-point to 98.5 p.c., also at the boiling-point. Examples are given of the use of these graphs in designing apparatus for concentration plant.

A complete and very detailed illustrated description of the Gaillard concentrating plant as developed by Kynoch, Ltd., in England and Natal, is given by Parkes and Coleman (J. Soc. Chem. Ind. 1921, 40, 257). The main tower 10 ft. by 48 ft. and a recuperating tower 4 ft. 6 ins. by 30 ft. heated by the waste gases from the main tower are employed. With a fuel consumption of 13–14 p.c., a feed acid of 70 p.c., and a finished acid of 95.5 p.c. the output of the system is 30 tons per 24 hours. If the finished acid is 92–93 p.c. the output is 40 tons. Obsidianite was used for the main tower and the recuperator, but several other kinds of acid proof brick proved equally satisfactory. The best cement for laying the brick was found to be that of Chance and Hunt (Eng. Pat. 119966, 1919).

Experiments on the use of the Cottrell process for the precipitation of fumes from a Gaillard concentration plant have been carried out by Kaltenbach, who gives his results and conclusions as to the conditions of successful working (Chim. et Industrie, 1921, 5, 143).

Barth (D. R. P. 304343, 1920) suggests the evaporation of sulphuric acid in an apparatus provided with walls down which the acid flows. Cross-walls with openings not in alignment act as baffles for the hot gases.

Pauling (D. R. P. 299774, 1920) uses a rectifying column apparatus of rather complicated design.

Sulphuric acid of 100 p.c. H_2SO_4 is usually obtained by adding fuming acid to ordinary oil of vitriol; this was formerly a very expensive process, and Lunge worked out a method for freezing out the acid from ordinary concentrated sulphuric acid by suitably cooling it, separating the crystals from the fluid portion and melting the former (Eng. Pats. 96, 1883; 4430, 1887). It was worked for a number of years in England at Widnes, and on the Continent at Petti-Quevilly

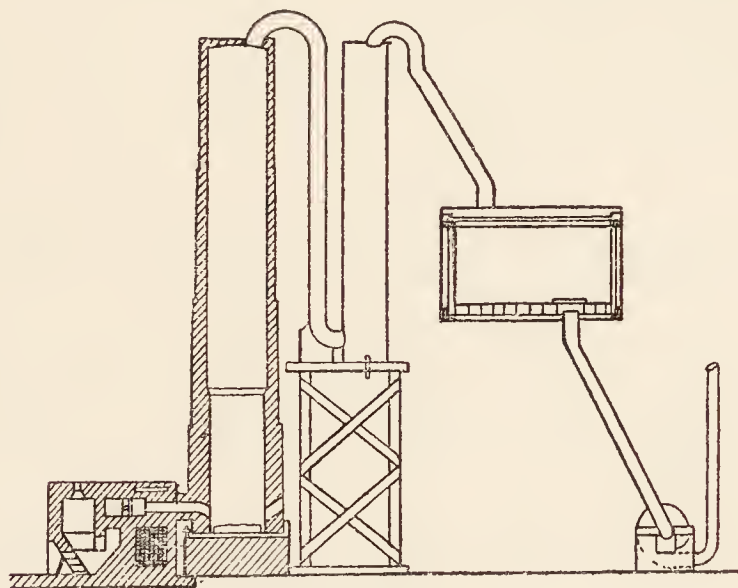


FIG. 16.

and Griesheim, but it has been given up owing to the cheapening of fuming acid. It is described by Lunge (Sulphuric Acid, vol. i. 918) and by Osterberger and Capella (Bull. Ind. Soc. Rouen, 1889, 307).

PRACTICAL YIELD OF SULPHURIC ACID AND LOSSES DURING MANUFACTURE.

100 parts of sulphur charged into the kilns as brimstone or pyrites should theoretically yield 306.25 parts H_2SO_4 . This yield is never obtained in practice, the chief sources of loss being—

(1) Sulphur is left in the ashes or cinders as sulphide, sulphate, &c. In the case of brimstone this is usually negligible, but with pyrites the sulphur left in the burnt ore may vary from 1 p.c. in the case of certain non-cupreous ores, practically free also from lead and zinc, to 2.5–3 p.c. in ordinary cupreous Spanish ores (Rio Tinto, Tharsis, Esperanza, &c.), and may reach 7 or 8 p.c. in the case of inferior ores containing much lead or zinc, or with good ores owing to faulty construction or working of the burners.

(2) Sulphur may sublime, when it will condense in the flues or in the acid itself and is lost.

(3) Loss occurs by leakages of gas during charging and working the kilns, potting nitre, and through cracks and holes in the chamber walls due to corrosion if they are not kept in good repair; and by leakages of liquid acid from chambers, siphons, tanks, &c.

(4) Sulphur escapes in the exit gases either

through incomplete conversion of sulphur dioxide into sulphuric acid, or by incomplete condensation of the suspended vesicles of the latter substance.

Loss by incomplete conversion mainly depends in the first place whether Gay-Lussac towers are used or not; if they are used the sulphur dioxide escaping cannot amount to more than 2 p.c. of that equivalent to the sulphur burnt without causing a great loss of nitre through the formation of much nitric oxide, and it may be kept below 1 p.c. if the chamber space is ample (18–20 feet per lb. of sulphur burnt), the Gay-Lussac tower is well-proportioned and carefully packed, and the working of the whole process is under skilled supervision.

Under such conditions 100 parts of sulphur (as pyrites) charged into the kilns may be accounted for thus—

Left unburnt in 'cinders'	5–6 parts.
Losses through leakages and incomplete conversion	2 3 „
Total losses	7–9 „

leaving 93–91 parts obtained as sulphuric acid, which is equivalent to 285–278 parts H_2SO_4 per 100 sulphur charged.

Even where only 11–12 cub. ft. chamber space per lb. sulphur burnt is employed, as good a yield may be obtained, provided that the capacity of the absorbing towers is considerably increased.

From brimstone 295–300 parts may be obtained per 100 sulphur charged, losses from incomplete burning being usually insignificant.

Where no Gay-Lussac tower is used the loss from incomplete conversion and condensation may be much greater, even when 25–30 cub. ft. chamber space per lb. sulphur is employed.

Consumption of nitre.—As regards loss of nitre both with and without Gay-Lussac towers, the figures obtained in different factories vary very considerably; but, in general, the nitre used per 100 parts of sulphur burnt varies between 2·5 and 4 p.c.,¹ where Gay-Lussac towers are employed, and averages about 10 p.c. when they are absent. The more recent improvements of the chamber process have resulted in a great increase in the capacity of the chamber plant in many instances without any serious increase in nitre consumption.

Guttmann (J. Soc. Chem. Ind. 1903, 1332) states that Meyer, for his circular chamber system, guarantees a maximum consumption of 2·7 p.c. nitre, using 11·6 cub. ft. chamber space per lb. of sulphur burnt; with intermediate towers, fans and atomised water in place of steam, this may be reduced to 1·8 p.c. nitre.

Lüty (Zeitsch. angew. Chem. 1905, 1253), in describing Niedenführ's system, states that with 7–9 cub. ft. chamber space only 2·2–2·45 p.c. nitre is required.

The Alkali Works Report for 1906 gives particulars of a chamber system in which steam has been completely replaced by atomised water, whereby the chamber space has been

reduced from 16·2 to 10·33 cub. ft. per lb. sulphur, and the nitre consumption from 4·23 to 2·87 p.c.

Littmann (Zeitsch. angew. Chem. 1906, 1177) claims that by allowing the gas from the Glover tower to enter the first chamber by six inlets at intervals along the top instead of by one at one end, he was able to reduce the chamber space from 14·5 to 12·9 cub. ft., and the nitre consumption from 3·6 to 2·9 p.c.

Falding (Eng. and Mining J. 1909, 441), in describing his system in which he combines one large chamber of considerable height compared with its length or breadth, with a cooling tower before the Gay-Lussac tower (U.S. Pat. 932771, 1909), states that with a chamber space of 7 cub. ft. per lb. of sulphur burnt, he only uses 2·8 p.c. nitre, and later (J. Ind. Eng. Chem. 1913, 223) he states that the chambers can be worked with only 1 to 1·5 p.c. nitre, using the same chamber space. On the other hand, Nemes (Zeitsch. angew. Chem. 1911, 387) adversely criticises the intensive system of working, and contends that the nitre consumption invariably rises with, and much more rapidly than, the yield per cubic metre; more supervision is required, and the cost of production of the acid is increased. He gives figures which differ considerably from the results quoted above.

Petersen (Zeitsch. angew. Chem. 1911, 877) replies to Nemes, giving the results obtained by Falding's and Meyer's systems in order to refute his statements.

Hasenclever (J. Soc. Chem. Ind. 1911, 1291), in the Hurter memorial lecture, gives it as his opinion that 11 cub. ft. per lb. of sulphur burnt is about the limit for chamber space without unduly increasing the cost of chamber repairs.

The nitre consumption in the Opl tower process as worked at Hruschau is given by Hartmann (Zeitsch. angew. Chem. 1911, 2303) as equal to 2·25 p.c. on the sulphur burnt, whilst the reaction space of the system is 0·53 cub. ft. per lb. 1·7 acid (approx. 2 cub. ft. per lb. sulphur).

Petersen (Zeitsch. angew. Chem. 1912, 762) compares the tower system with Falding's to the advantage of the latter.

MANUFACTURE OF FUMING ACID.

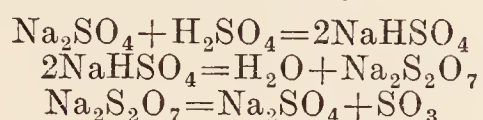
The various processes for the production of fuming acid, which have been at different times patented and put more or less in actual operation, may conveniently be grouped in two divisions—namely: (1) those depending on the action of heat on some metallic sulphate, whereby decomposition is brought about with evolution of sulphur trioxide, more or less further decomposed into sulphur dioxide and oxygen according to the temperature employed; (2) those in which the essential action is the surface or catalytic action of certain solids in bringing about union between sulphur dioxide and oxygen.

(1) PROCESSES OF DISTILLATION OF SULPHATES.

The substance most largely employed, before the development of the contact process, as a source of fuming acid, was sulphate of iron, formerly in the form of 'copperas' or 'green vitriol' (ferrous sulphate), carefully dried so as to

¹ On the Continent the consumption of nitre is stated in a number of different ways. Usually the percentage is calculated on the acid made either in the form of chamber acid, acid of 1·7 sp.gr. or 100 p.c. H_2SO_4 . Frequently it is stated in terms of nitric acid of 1·33 sp.gr., instead of sodium nitrate.

deprive it of most of its water of crystallisation and partially peroxidised during the process; latterly in the form of crude ferric sulphate prepared by long-continued weathering of certain slaty minerals containing iron sulphide disseminated throughout them, lixiviation of the mass, evaporation of the mixed ferrous, ferric and aluminium sulphates dissolved out, and gently roasting so as to dehydrate the mass and completely peroxidise the iron present. The product thus obtained was heated in a series of clay retorts mounted together in a large 'galley' furnace, the sulphur trioxide was expelled and condensed in receivers previously charged either with a small quantity of water or preferably with oil of vitriol or weak fuming acid from a previous operation. This process was worked in Bohemia from about the year 1790 until 1900, when it was given up, as it could not compete with the 'catalytic' or 'contact' process. Sodium pyrosulphate obtained by carefully heating sodium hydrogen sulphate, was proposed by Prelier in 1847, and repatented by Wallace in 1876; the reactions here are



so that the process is a continuous one, the neutral sodium sulphate resulting from the distillation being converted into sodium hydrogen sulphate by treatment with sulphuric acid, and so on, over and over again. Wolters mixed magnesium sulphate with the pyrosulphate, stating that the sulphur trioxide was given off at a lower temperature than with pyrosulphate alone. Cummings (Eng. Pat. 7355, 1886) heated bricks made of gypsum and clay in a kiln, whereby silicate of lime and alumina were formed, suitable for hydraulic cement, while sulphur trioxide was evolved, more or less decomposed into sulphur dioxide and oxygen.

(2) CATALYTIC OR CONTACT PROCESS.

It has long been known that when a mixture of sulphur dioxide and oxygen is passed through a tube containing heated platinum, combination is induced, and sulphur trioxide formed; Peregrine Phillips, a vinegar maker, of Bristol, was the first to utilise the reaction in vitriol-making, and so to dispense with the use of nitre; in 1831 he patented a process of this kind (Eng. Pat. 6096, 1831), brimstone being burnt in excess of air, so that the gaseous mixture contained sufficient oxygen, and the gases were passed through heated tubes containing finely-divided platinum. The sulphuric acid formed was absorbed in a lead-lined tower filled with pebbles, down which water trickled. The process proved unable to compete with the chamber process at the time, and the demand for fuming acid had not yet arisen. Nevertheless, Phillips must be recognised as the real inventor of the contact process which has made such enormous progress during the last 30 years, having superseded all other processes for the manufacture of fuming acid, and is also largely employed for the production of high strength non-fuming acid in place of the lead chamber process.

Although several other attempts were made to utilise the catalytic action of platinum for this purpose no real progress was made until the year

1875, when two proposals were brought forward for manufacturing fuming acid by catalytic action. In that year Squire and Messel (Eng. Pat. 3278, Sept. 18, 1875) invented a process for the manufacture of sulphur trioxide and fuming acid, in which ordinary oil of vitriol was decomposed by heat into sulphur dioxide, oxygen, and steam, the latter was removed by condensation, as in Deville and Debray's process for the manufacture of oxygen from vitriol, except that the sulphur dioxide was not removed with the aqueous vapour, and the sulphur dioxide and oxygen were recombined by passing over heated platinised pumice (The Alkali Trade, C. J. Kingzett, p. 25). In 1875 also Winkler (Dingl. poly J. Oct. 1875, 128) suggested a process based on much the same lines in which platinised asbestos (prepared by dipping asbestos successively into platinic chloride and sal-ammoniac solutions and igniting) was to be employed as the 'catalytic' agent. The principal difficulty in applying this process industrially was the rapid corrosive action exerted upon that part of the plant where the sulphuric acid was decomposed by heat. Squire and Messel's process was started at Silvertown in April, 1876, and was worked for a number of years until superseded by other processes mentioned later.

Fuming acid was made in Germany also by this or a similar method in 1877 by Clemm at Mannheim, and later by Jacob at Kreuznach, and in 1882 by Meister Lucius and Brüning at Höchst. In 1881 at the Thann Chemical Works in Alsace, a process introduced by Squire and worked out during 1879-1880 in conjunction with Chapman, Messel & Co. of Silvertown, was started for the manufacture of fuming acid from brimstone burner gases. The latter were treated with water under a pressure of 4 atmospheres. The sulphur dioxide was expelled by steam, mixed with air and passed over heated platinised asbestos. The sulphur trioxide formed was absorbed by concentrated sulphuric acid, and the exit gases containing some unoxidised sulphur dioxide were passed back into the process. Soon afterwards a similar plant was started at Silvertown.

In 1878 Winkler (D. R. P. 4566) patented the use of a variety of catalytic agents of high activity, more especially such substances as asbestos, slag wool, infusorial earth, &c., or even organic bodies like cellulose or cotton wool, impregnated with platinum black by soaking in platinum chloride solution and reducing with sodium formate. Messel (1878) patented the employment of sulphur dioxide and oxygen made by burning sulphur in excess of electrolytic oxygen. A somewhat similar patent was taken out by Lunge in 1888, pure oxygen obtained by Brin's process being employed. Neale (Eng. Pat. 1103, 1876) heated anhydrous sulphates or bisulphates in earthenware retorts and passed the mixture of sulphur dioxide and oxygen thus obtained over heated platinised asbestos, spongy platinum, or the oxides of iron, chromium, or copper. In 1882 Rath took out a patent for the use of ordinary burner gases from sulphur or pyrites burnt in air, passed through purifiers for removing dust and aqueous vapour, and then through vertical iron tubes containing surface-acting materials at a temperature below a full and a red heat. And in

1887 Hänisch and Schröder (Eng. Pat. 9188) worked out a process in which 25 p.c. pure sulphur dioxide, obtained by treating burner gases with water in a coke tower and expelling the sulphur dioxide by heat, as in their process for the manufacture of liquid sulphur dioxide, with 75 p.c. air were passed over heated platinised asbestos while under a pressure of 2–3 atmospheres. According to Lunge, this process was at work for some years in several large factories until the development of the contact process dealing with ordinary pyrites gases made it unprofitable.

In 1898 patents were taken out almost simultaneously by the Badische Anilin und Sodafabrik, by Meister Lucius and Brüning of Höchst, and by the Mannheimer Verein Chemischer Fabriken, for the manufacture of sulphur trioxide from ordinary pyrites gases by the contact process. They have been followed from time to time by other patents, giving particulars of later developments of these processes.

The best-known of these is that of the Badische Anilin und Sodafabrik (Eng. Pats. 15947, 15948, 15949, 15950, 1898). These patents give a general description of the process, and more details have been furnished by Dr. Knietsch in a lecture before the German Chemical Society (Ber. 1901, 4069). The pyrites burner gases have first to be purified from all substances that can affect the activity of the platinum of the contact mass. Arsenic, phosphorus, and mercury are the most injurious and the most difficult to remove from the gases; other substances may also do harm either by mechanically enveloping the platinum or by chemically affecting it, are iron, lead, copper, antimony, &c.

The gases are first treated with a jet of steam in the dust flue; this helps to oxidise any sulphur which has sublimed, by thoroughly mixing the gases, and at the same time it moistens them and prevents any condensation of concentrated sulphuric acid in the cast-iron cooling pipes, and therefore the possible formation of gaseous arsenical compounds, such as arsenuretted hydrogen, which cannot be eliminated when once formed, and which find their way into the contact mass, and in time seriously diminish its activity. The gases are then cooled to 100°C . by water in a tubular lead cooler, the steam again serving a useful purpose by preventing the formation of hard crusts in the cooler, and by diluting the condensing acid to such an extent that it has no serious action on the leaden tubes. The gases are next repeatedly washed with water or dilute sulphuric acid to free them from all traces of mist or dust, and are finally dried by means of concentrated sulphuric acid. Before passing to the contact apparatus they are examined optically, to see that they are free from dust and mist, by looking through a layer some yards in length illuminated at the further end, and chemically by allowing a stream of the gas to bubble through water for 24 hours, and then examining the liquid for arsenic by the Marsh test. The sulphuric acid mist must be completely removed, as it acts as a carrier for arsenic and other injurious substances.

The pure and dry gas, containing about 7 p.c. SO_2 , is next forced by means of a mechanical mover through the contact apparatus, one form of which is shown (Fig. 17). This consists

of a number of narrow vertical iron pipes containing the contact substance, in an outer casing also of iron. A portion of the gas enters this outer casing near the bottom, passes up between the contact tubes to a chamber at the top, where it meets and mixes with the remainder of the gas which enters the apparatus there. The temperature of this mixture is regulated by the relative proportions admitted at top and bottom, and should be high enough to start the reaction when it reaches the platinum contact material. The mixed gases pass down through the contact

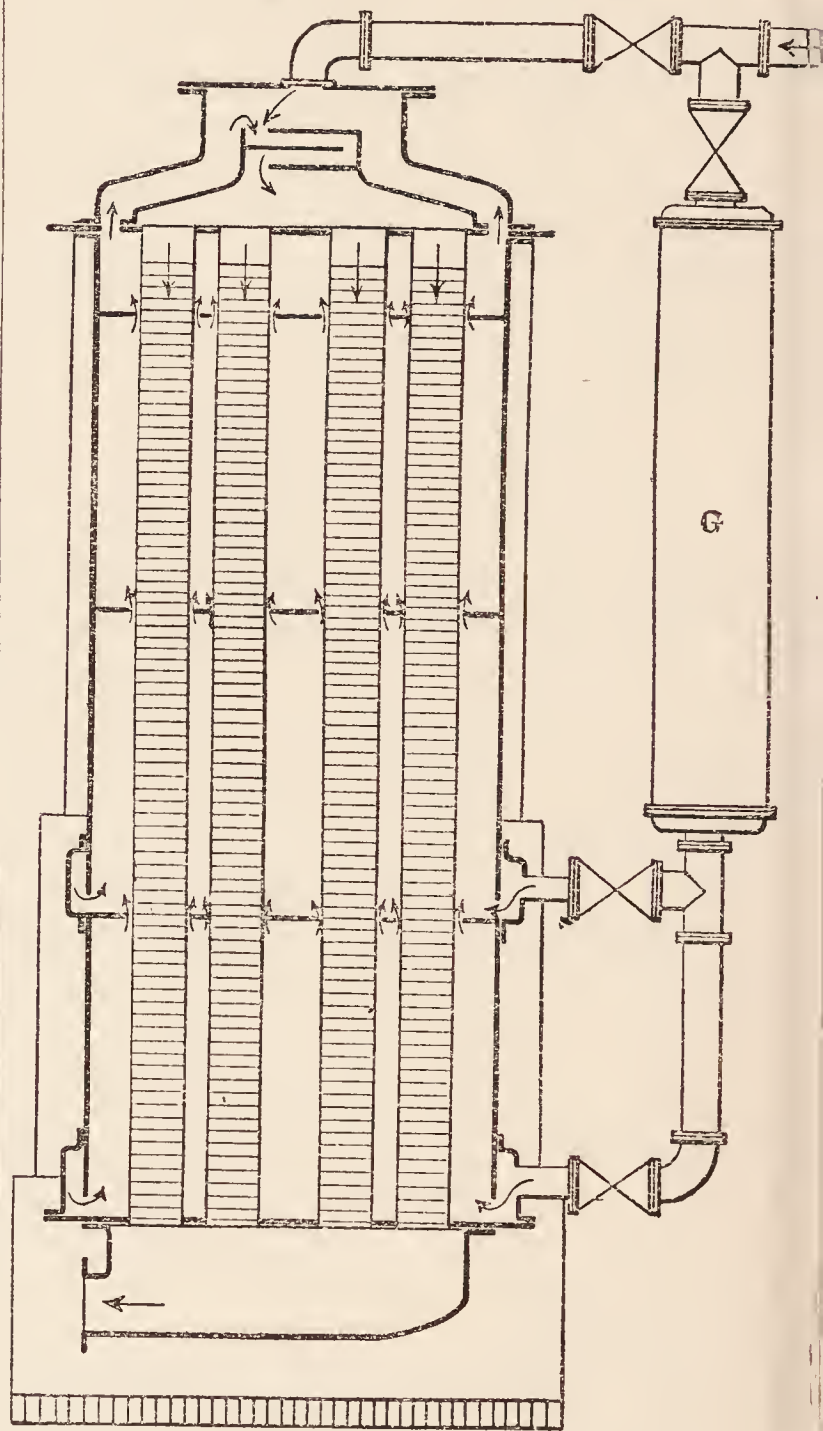


FIG. 17.—CONTACT APPARATUS.

tubes, and the temperature rises quickly owing to the rapidity with which the combination of sulphur dioxide and oxygen takes place, but it is kept from rising too high by the stream of gas passing up between the tubes from below. When sulphur dioxide and oxygen combine to form sulphur trioxide, 32,200 calories are set free, and unless it is checked, the temperature rises so high that the reverse action sets in, the sulphur trioxide being decomposed again into sulphur dioxide and oxygen. A portion of the gas may also be admitted at different levels into the apparatus in order to get the best regulation of the temperatures. If necessary the gases are heated before entering the apparatus by their passage through the tubular heat-interchanger

or regulator, through which a portion of the hot gases leaving the contact apparatus pass.

The contact material consists of platinised asbestos containing about 10 p.c. platinum, and it is arranged in each vertical tube on perforated plates strung on a central rod, and separated from each other by short lengths of pipe in order that it should not get compressed and offer any considerable resistance to the passage of the gases.

The apparatus is first heated to above 300°C. in some convenient way, and the purified gases are then allowed to enter, the amounts, passing in at various levels, being regulated by the temperatures registered by thermometers at the top and bottom of the apparatus. The gases should reach the contact material at a temperature between 300° and 400°. The energetic action taking place at first causes a rapid rise to over 500°, followed by a gradual cooling, so that the gases leave the contact material at between 400° and 450°, at which temperatures a conversion of 96–98 p.c. may be obtained. The most suitable temperatures for maximum conversion will depend on a number of different factors, namely the quantity of gas passing through the apparatus, the percentage of sulphur dioxide and oxygen in the gases, the efficiency of the contact material, &c.

Other substances may be used instead of asbestos in combination with platinum as contact material. A mixture of salts consisting of a non-volatile base or salt of a non-volatile base which contains a radicle of a volatile acid, with a salt of a volatile base and non-volatile inorganic acid may be incorporated with platinum chloride and heated (Eng. Pat. 6828, 1901). Or oxides of iron, copper, or chromium may be used as foundations for the platinum (D. R. P. 140353, 1901). Two contact apparatus may be employed, 80–90 p.c. conversion being obtained in the first, and the action completed in the second, the sulphur trioxide being removed from the gases before passing into the second apparatus. By this means the quantity of platinum employed may be considerably reduced (Eng. Pat. 12781, 1901).

The absorption of the sulphur trioxide takes place in iron vessels, wrought iron being used for making fuming acid, and cast iron for ordinary concentrated sulphuric acid (Eng. Pats. 1904, 1901, and 6829, 1901). Fuming acids containing more than 27 p.c. free sulphur trioxide have practically no action on wrought iron; by passing the gases through an absorber of this material, provided with a serrated hood dipping into acid of this strength or higher, and fed with dilute acid, fuming acid may be continuously obtained practically free from iron (containing less than 0.003 p.c.). To complete the absorption of the sulphur trioxide a similar absorber of cast iron is employed, also fed with dilute acid, but kept at a strength of between 97 and 98 p.c. H_2SO_4 , at which strength almost perfect absorption may be obtained. If the attempt be made to absorb the sulphur trioxide with weaker acids or water, a considerable amount of white acid fume escapes from the apparatus, even although a number of absorbing vessels be employed.

McDavid has determined the vapour pressure of fuming sulphuric acid containing from 0–45 p.c. free sulphur trioxide for temperatures between 40° and 90°, and the results

are reproduced in graphical and tabular form. Across the graph of the vapour pressure curves a number of horizontal lines, denoting the percentage concentration by volume of sulphur trioxide corresponding with the pressures in mm. of mercury, have been drawn, so that it is possible to read off directly the maximum strength of fuming sulphuric acid that can theoretically be produced from any gas, at any temperatures within the range given above. These data indicate the number of absorption vessels required for complete absorption of sulphur trioxide from the gases issuing from the contact plant. The course of the absorption depends on the total weight of sulphur trioxide entering the apparatus in a given time, its concentration in the gas entering the system, the strength of the fuming sulphuric acid being produced, the strength of the acid fed into the last absorption vessel, and the temperature. The results obtained on a large-scale absorption plant agree very closely with those calculated by the method described in the paper (McDavid, J. Soc. Chem. Ind. 1924, 43, 57; Chem. Soc. Abstr. 1924, 126, ii. 330).

Further details of the Badische process are given in U.S. Pats. 690062, 1901; 692018, 1902.

The processes worked out by Meister Lucius and Brüning of Höchst are described by Dr. Krauss and von Berneck in Lunge's *Sulphuric Acid and Alkali*, vol. i. 1374, and in various patent specifications. In their earlier process, the pyrites kiln gases were freed from impurities by washing with water, &c., dried by concentrated sulphuric acid and heated in a contact apparatus consisting of preliminary heating pipes and two contact retorts containing platinised asbestos. The gases left the contact apparatus at 400°–450°, and the sulphur trioxide was absorbed by concentrated sulphuric acid in cast-iron absorbers. After working in this way for some years, improvements were made by utilising the heat of the reaction for heating the incoming gases (Eng. Pat. 6057, 1898) and for regulating the temperatures of the contact apparatus by the introduction of cold gases at various parts (Eng. Pat. 285, 1899). The greatly increased velocity of the reaction at high temperatures, up to a certain stage of the combination, next led to improvements for working the process, first at a high temperature, 530°, to obtain 75–80 p.c. conversion, and then at a lower temperature, 400°–450°, to complete it, either by working with two contact chambers kept at different temperatures, with cooling arrangements between, or by employing a long contact space, in which the gases enter at 530° and leave at about 430° (Eng. Pat. 1385, 1901). If two contact chambers are employed, a cheaper catalyst than platinum may be used in the first. The following list of active catalytic agents is given in this patent specification.

1. Platinum group metals.
2. Oxides and sulphates of Fe, Cr, Ni, Co, Mn, Ur, Cu.
3. Oxygen compounds of Al, Be, Zr, Ce, Di, La, Th, Ti, Si, and nearly all rare metals.
4. Mixtures of 1 with 2 and 3.
5. Mixtures of two or more substances of 2 and 3.

2, 3, and 5 can only be used at high temperatures, and hence may be used in the hot part of the contact apparatus. Other contact materials have been suggested. Farup employs iron and titanium (D. R. P. 263392, 1912; U.S. Pat. 1219277), Ellis (Eng. Pat. 110776, 1916). The Badische Co. propose vanadium oxide (Eng. Pat. 23541, 1913); mixtures containing tin and chromium (U.S. Pats. 1204141/2/3, 1227044, 1917); palladium with silver, gold, tungsten or molybdenum (J. Soc. Chem. Ind. 1917, 81); sulphates of thorium, cerium and praseodymium (D. R. P. 149677, 1903).

The removal of the sulphur trioxide from the gases before passing into the second contact chamber and the more perfect utilisation of the heat of the reaction by means of heat inter-changers in which the gases are cooled before the absorption of the sulphur trioxide and heated again for the completion of the reaction was the next improvement. Working in this way it is possible to use a cheaper catalytic than platinum in both contact chambers, which must be kept at the necessary high temperature, 80 per cent. conversion being obtained in the first, whilst 80 per cent. of the remaining 20 per cent. SO_2 is oxidised in the second, making 96 per cent.

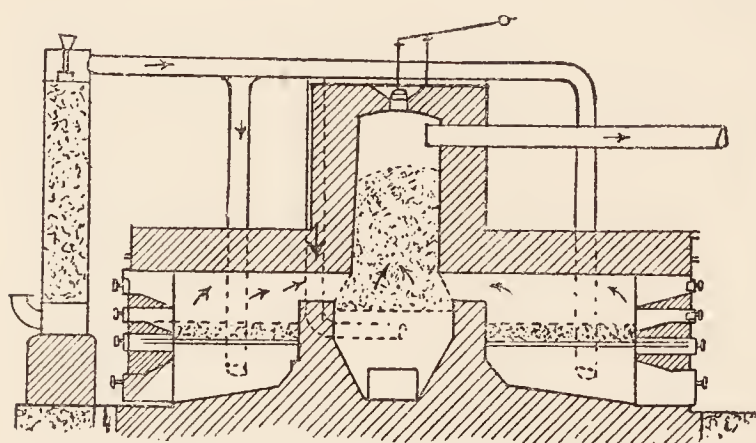


FIG. 18.

altogether; additional heat may also be obtained from the hot burner gas by passing the purified gas through a tubular economiser placed in the dust-chamber (Eng. Pat. 2368, 1901). Further particulars of the Höchst processes are given in Eng. Pats. 3161 and 4026, 1902; D. R. PP. 135887, and 169728, 1902.

In the process of The Mannheimer Verein Chemischer Fabriken (Eng. Pats. 17266, 1898; 1859, 3185, 24748, 1899; 12806, 1902; U.S. Pat. 690133, 1901) the air supplied to the pyrites furnaces is previously heated and dried, and the hot dry gases at about 700° pass at once into an iron-cased chamber containing ferric oxide (burnt ore) in pieces resting on a grate (Fig. 18). 60–65 p.c. of the sulphur dioxide is said to be here converted to sulphur trioxide, and at the same time the arsenic is retained by the oxide of iron. The latter is renewed from time to time as its catalytic activity diminishes. The gases pass on to an absorbing apparatus where the sulphur trioxide is removed, and are then forced by a fan-blast through filters of porous, granular, or fibrous substances to remove the last traces of impurities. They are now reheated before entering the final contact apparatus, which consists of a chamber containing removable iron frames supporting a net-work of platinised asbestos or other platinised fabric, in superposed compart-

ments where the combination is completed. The sulphur trioxide is then absorbed as before.

Copper oxide, chromium oxide, or manganese oxide or their sulphates may be used instead of ferric oxide as contact material for the hot gases (Eng. Pat. 4610, 1901).

Additional details of this process are given in a paper by Wilke (J. Soc. Chem. Ind. 1906, 4).

The Mannheim contact plant developed by Kynoch is minutely described by Parkes and Coleman (J. Soc. Chem. Ind. 1922, 41 100 T). An output of 102.2 tons of 20 p.c. oleum was secured from 40 tons pyrites of 47.5 p.c. S per week.

The chief features of the Schroeder-Grillo process (Eng. Pats. 25158, 1908; 17034, 1900; 10412, 1901) and its development are described in three papers read before the New York section of the Society of Chemical Industry (J. Soc. Chem. Ind. 1903, 348; also 1912, 723). The gases are purified by first cooling them to the ordinary temperature, passing them through scrubbers or washing towers fed with water or dilute acid, and finally through wet filters of large area containing a very fine coke packing or a fibrous material such as asbestos or cotton wool, and drying them by means of concentrated sulphuric acid. They are then preheated to 260° – 280° , and passed into the bottom of a chamber set over a fireplace. In this chamber the contact mass is spread on perforated iron plates superposed one above the other, separated by partitions with central openings, by which means the gases are thoroughly mixed before passing from one layer to the next. The contact material carrying 0.2 p.c. platinum is prepared by mixing solutions of a platinum salt with other soluble salts such as magnesium sulphate or a soluble phosphate, evaporating to dryness, and granulating. When heated in the contact apparatus the platinum separates and a very porous material is obtained; or platinum chloride may be mixed with a liquid or pasty material or a substance which melts in its own water of crystallisation, and the mixture dried in the contact apparatus by passing hot gases through it. The advantages claimed for this kind of contact material are that it is easily regenerated when its activity decreases by treating with water and regranulating, and that it offers little resistance to the passage of the gases. The heat is regulated so that the gases leave the contact apparatus at between 350° and 400° , and the sulphur trioxide is absorbed in a scrubbing tower after passing through suitable coolers (Curtis, J. Soc. Chem. Ind. 1918, 369 R).

At Freiberg (Lunge's Sulphuric acid, vol. i. 1409) the pyrites gases are purified exclusively by filtration (without any washing or drying apparatus) through a set of lead towers packed successively with coke, charcoal, wood shavings, and cotton wool. From the last tower the gases are aspirated by a fan-blast, and propelled into the contact apparatus, which consists of five horizontal retorts in a furnace heated by means of a gas producer. The contact material consists of platinised pumice or platinised unglazed porcelain containing 3–4 p.c. platinum. The temperature is kept between 440° and 460° , and the combination obtained varies between 45 and 90 p.c., depending on the percentage of sulphur dioxide in the gases. The sulphur

trioxide is absorbed in towers fed with concentrated sulphuric acid and the uncombined gases are treated in vitriol chambers.

In Rabe's process (Lunge's Sulphuric Acid, vol. i. 1415; Eng. Pat. 2337, 1901) the pyrites gases, after leaving the dust chamber, are sprayed with water in a porcelain-lined conduit, until the temperature is reduced to a point at which condensation of the fluid contents cannot yet take place, and then through a Glover tower fed with cold dilute sulphuric acid to cool them. They then pass through filter beds consisting of layers of granular coke of successively diminishing size, or through fibrous materials such as asbestos, the surface of which may be washed with water from time to time. The gases are thus obtained quite free from dust, and are further purified from non-neutral elements of a gaseous nature such as hydrogen chloride by means of bisulphites in granular form or in concentrated solution, and dried by concentrated sulphuric acid. The contact apparatus is a wide chamber containing platinised asbestos spread on sieves and the gases are heated up to the necessary temperature before entering it. The sulphur trioxide is absorbed in specially constructed reaction towers by concentrated sulphuric acid.

The Tentelew process as carried out at the Tentelew Chemical Works, Petrograd, is described in the British patents mentioned below. The burner gases after leaving the dust-chamber are cooled down to the ordinary temperature by passing down a circular tower built of lead surrounded by a water-jacket and cooled internally by means of a number of hollow vertical plates through which water continually flows (Eng. Pat. 14670, 1911). They next pass up through a filter of larger area packed with coarse coke and then down through a similar filter containing very fine coke which removes all acid mist. The purification is completed by passing the gases through a series of washers containing an aqueous solution of an alkali or milk of lime or other alkaline earth to remove gaseous impurities as HCl , SiF_4 , etc. (Eschellmann, Eng. Pat. 12213, 1907).

After drying, the pure gas passes through a heat interchanger or regulator to the contact apparatus. The first portion of the latter consists of a large empty vessel of considerable area, at the bottom of which is spread a layer of the contact material (platinised asbestos) on a perforated plate with projecting truncated pyramids which radiates its heat into the space above containing the incoming gases. By this means the temperature in the contact mass is not allowed to rise too high, and the conversion is completed in the lower narrower portion of the apparatus where the contact material is arranged in 25 thin layers on perforated plates and which is carefully protected against loss of heat (Eschellmann and Harmuth, Eng. Pats. 11969, 1902; 20952, 1904; 23419, 1909). After passing through the heat regulator again, and a small air cooler, the SO_2 is absorbed in a specially designed absorbing tower by concentrated sulphuric acid (Eschellmann and Harmuth, Eng. Pat. 22095, 1907).

A great many other patents have been taken out in recent years in connection with the contact process.

For purifying the burner gases Raynaud and Pierron (Eng. Pat. 16253, 1900) condense them in a porous material like kieselguhr, and after an interval expel them again by heat. The impurities are left behind. Eschellmann and Harmuth, U.S. Pats. 937147, 937148, recommend the use of coke filters for removing lubricating oil from the purified gases before allowing them to enter the contact chamber.

Herreshoff (U.S. Pats. 940595, 950596, 955067, 969868, 1910) describes methods for cooling and purifying the burner gases by bringing them into intimate contact with weak acid in scrubbing towers and cooling pipes.

Messel (Eng. Pat. 22672, 1909) passes the burner gases over granulated coke or other carbonaceous material at a temperature above 300° in order to reduce any sulphur trioxide or sulphuric acid present to sulphur dioxide. In this way the acid mist which acts as a carrier for impurities is decomposed, and the whole of the sulphur dioxide and sulphur trioxide originally in the gases is obtained as sulphur trioxide and sulphuric acid in a pure condition (Heinz, U.S. Pat. 875909, 1908).

Herreshoff (U.S. Pats. 719332 and 719333, 1903) employs two or more contact chambers with heat interchangers between. Ferguson (U.S. Pats. 723595, 723596, 1903) recommends the introduction of air into the gases in the interchangers to increase the content of oxygen, and (U.S. Pat. 857389, 1907) describes a long narrow contact apparatus furnished externally with ribs between which asbestos can be packed to regulate cooling by external air.

Raynaud and Pierron (Eng. Pat. 16254, 1900) suggest the use of different strengths of platinised asbestos in different parts of the contact apparatus in order to keep the temperature uniform. For absorption of sulphur trioxide, Herreshoff (U.S. Pats. 737233, 737626, 722981, 1903) describes apparatus suitable for this purpose.

Contact substances.—The most important of these is platinised asbestos. It may be prepared of any strength up to 80 p.c. platinum by soaking asbestos in an alkaline solution of platinum chloride mixed with sufficient sodium formate to reduce the platinum, and heating to 70° – 80° . The platinum black is precipitated on the fibre, and the salts can be washed out with water without removing any of the platinum.

Another method of preparing it is by soaking the asbestos with a mixture of platinum chloride solution and methylated spirit, and setting fire to it.

Many other substances besides asbestos have been suggested as carriers for the platinum. Pumice, porcelain, oxides and sulphates of iron, copper, and chromium, soluble sulphates and phosphates have already been mentioned. Others are clay, glass wool, kieselguhr, and sulphates of barium and calcium.

Revivification of inactive platinum contact masses.—The Badische Anilin and Sodafabrik (D. R. P. 148196) treat the contact mass with dry sulphur dioxide or purified burner gas containing an excess of sulphur dioxide and little oxygen at the temperature of the contact process to remove arsenic and other impurities; or else with gases containing volatile compounds of chlorine.

D. R. P. 135887, 1902, recommends the

which a quantitative conversion is not obtainable.

The formula of conversion should be written $2\text{SO}_2 + n\text{O}_2 = 2\text{SO}_3 + (n-1)\text{O}_2$, where n should not be less than 2.

Taking a technical burner gas containing 7 p.c. SO_2 , 10 p.c. O_2 , and 83 p.c. N_2 , which is passed through a porcelain tube containing platinised asbestos heated to various temperatures, it is found that the first trace of sulphur trioxide appears at a little above 200° , and that the conversion is practically complete about 400° , and remains so up to 430° . Above this temperature the sulphur trioxide gradually dissociates more and more as the temperature rises, till it is all again reduced to sulphur dioxide and oxygen at 900° – 1000° (curve 1, Fig. 19).

On increasing the rate of flow of the gas, or decreasing the amount of platinum employed, the maximum percentage conversion obtainable decreases, but at the same time the temperature of maximum conversion increases, but in all cases there is the gradual reversion of the reaction which becomes complete at between 900° and 1000° as before (curves 2, 3, 4 and 5). Between 200° and 450° the reaction of formation preponderates, but above 450° the dissociation of sulphur trioxide comes very rapidly into play.

If the gases are passed through an empty porcelain tube some combination takes place, a maximum conversion of 30 p.c. being obtained at 600° (curve P), but if we start with almost completely converted gases and pass them through a heated empty tube, we find that decomposition only begins to take place as the temperature approaches 800° , and is not quite complete even at 1200° , thus showing that sulphur trioxide, once formed, is very stable at high temperatures in the absence of an active contact substance (curve D). If the tube is filled with pieces of porcelain the decomposition begins earlier and increases more rapidly as the temperature rises (curve E), but not to the same extent as in the presence of platinum. Knietzsch concludes from the results of his experiments that only those contact substances will be able to produce a quantitative reaction in one operation which exhibit their maximum of activity below 450° . All substances such as oxide of iron which develop their maximum power only beyond this temperature can never produce a quantitative conversion of sulphur dioxide into sulphur trioxide, no matter how long they remain in contact with the gases. Up to now there is only one catalytic substance which fulfils the before-mentioned conditions, and that is platinum, and it cannot be replaced by any other metal of the Pt group with even approximately equivalent results. On the other hand, above 450° the velocity of the reaction increases rapidly as the temperature rises, so that a large amount of sulphur dioxide may be converted to sulphur trioxide by a small amount of platinum when working at a high temperature, although the conversion may not be more than 90 p.c., and then the reaction may be completed at a lower temperature by using a larger amount of platinum. Fig. 20 represents this increase in velocity with temperature very clearly. Or a cheaper catalytic such as oxide of iron may be employed in the first stage of the operation.

Brode (Zeitsch. angew. Chem. 1902, 1081) applies the laws of chemical equilibrium and velocity of reaction to the contact process and shows that to increase the reaction velocity and carry the reaction further towards completion, increase of sulphur dioxide and oxygen concentration and decrease of sulphur trioxide concentration are necessary.

The formula $K = \frac{C_{\text{SO}_3}^2}{C_{\text{SO}_2}^2 \times C_{\text{O}_2}}$ shows that the

ratio of sulphur trioxide to sulphur dioxide increases as the square root of the oxygen concentration. Also as the formation of sulphur trioxide lessens the volume, it must be favoured by increase of pressure.

Bodländer and Köppen (Zeitsch. Elektrochem. 1903, 559) state that in the reversible reaction $2\text{SO}_2 + \text{O}_2 \rightleftharpoons 2\text{SO}_3$ equilibrium is represented by $\frac{(\text{SO}_2)^2(\text{O}_2)}{(\text{SO}_3)^2} = K$, and depends only on

the relative concentrations of the reacting bodies, but the velocity depends on the absolute concentrations. Thus dilution with extra air retards the reaction at first, while it is rapid, but greatly accelerates it in the later stages.

By heating gaseous mixtures in a tube with platinum gauze, and measuring the diminution of pressure at constant volume, these chemists find that at temperatures between 182° and 341° the values of K approximate more nearly to $[(\text{SO}_2)^2 \cdot (\text{O}_2)]$ than $[(\text{SO}_2) \cdot (\text{O}_2)]$ and that the velocity increases about 1.4 fold for each 10° rise in temperature. Also the concentration of the sulphur trioxide formed retards the reaction even at these low temperatures.

They also have determined the temperatures at which, with different gaseous mixtures of sulphur dioxide, oxygen, and nitrogen, definite percentages of the total possible amount of sulphur trioxide will be formed, when equilibrium is established. Above 650° the platinum absorbs oxygen.

Comp. of orig. mixture		Yield of SO_3						
SO_2	O_2	98 p.c.	96 p.c.	94 p.c.	92 p.c.	90 p.c.	80 p.c.	60 p.c.
At atmospheric pressure		°C.	°C.	°C.	°C.	°C.	°C.	°C.
66.6	33.3	425	476	497	520	538	597	668
11.69	5.85	378	423	452	473	489	543	553
10.0	8.04	450	483	503	518	531	576	635
8.0	10.62	467	505	518	537	548	592	648
7.0	10.0	467	504	518	535	547	590	647
6.0	13.23	477	513	530	545	557	602	658
4.0	15.81	483	521	539	554	565	611	666
2.0	18.45	488	527	543	558	570	615	671
At 10 atmospheres pressure								
11.69	5.85	428	477	504	527	543	605	680
10.0	8.04	503	538	558	576	589	639	703

Lucas (Zeitsch. Elektrochem. 1905, 457) repeated Bodländer and Köppen's experiments, and practically confirmed their results.

Bodenstein and Pohl (*ibid.* 1905, 373) adopted Knietzsch's method of passing a stream of sulphur dioxide and air or oxygen over platinum in a quartz tube heated by an electric furnace, and determining the composition of the mixture before and after contact. They have also calculated from their results and tabulated the yields (percentage of SO_2 converted to SO_3) for different mixtures at different temperatures.

Bodenstein and Fink (*Zeitsch. physikal. Chem.* 1907, 1) describe further experiments dealing with the kinetics of the contact sulphuric acid process.

A large number of papers have also been published dealing more particularly with the ferric oxide contact process.

Keppeler (*Zeitsch. angew. Chem.* 1902, 809); Lunge and Pollit (*J. Soc. Chem. Ind.* 1903, 79); Lunge and Reinhardt (*Zeitsch. angew. Chem.* 1904, 1041); Kuster (*ibid.* 1904, 1512); Keppeler (*ibid.* 1908, 532, 577).

A series of articles relating to the manufacture of sulphuric acid by the contact process have appeared in *L'Ind. Chim.* during the year 1924.

STATISTICS OF THE PRODUCTION OF SULPHURIC ACID.

The *Chemische Industrie* of Feb. 1, 1912, attempts to estimate the quantity of sulphuric acid produced in the chief countries of the world from the consumption of pyrites. Taking the years 1900-1910 it will be seen that in the four most important industrial countries, England, France, Germany, and the United States, the consumption of pyrites in the last two countries during that period has steadily increased, while in England it has been practically stationary.

PYRITES CONSUMPTION IN 1000 TONS.

	England	France	Germany	United States
1900	753	397	627	536
1901	693	461	646	640
1902	620	423	647	645
1903	745	408	690	660
1904	753	426	678	620
1905	710	518	737	768
1906	770	589	776	858
1907	779	614	938	903
1908	777	592	878	890
1909	799	508	890	902
1910	801	—	1008	1007

Assuming a yield of 134 parts H_2SO_4 from 100 parts pyrites the sulphuric acid produced in 1910 would amount in tons to—

England	Germany	United States
1,073,000	1,350,000	1,349,000

To these figures must be added the amount of acid produced from brimstone, spent oxide, sulphuretted hydrogen, zinc blende, &c.

According to the 25th Alkali Report the quantity of brimstone burnt in England in 1883 was 17,295 tons equal to about 50,000 tons H_2SO_4 , and it will, no doubt, be less now. For spent oxide no figures are at present available.

In 1910 the consumption of zinc blende in Germany was 430,000 tons, from which the

greater part of the sulphur was utilised for sulphuric acid manufacture.

In France the production of sulphuric acid averaged about 900,000 tons during the last few years, and in Italy about 400,000 tons per annum.

In Russia in 1910 the production was 200,000 tons.

According to Wedge (*Proc. 8th Int. Cong. Appl. Chem.* 1912, 271, and *J. Soc. Chem. Ind.* 1912, 874) the production of sulphuric acid in the United States in the year 1911 amounted to 3,250,000 tons $50^\circ\text{Be}'$. = approx. 2,031,200 tons H_2SO_4 .

Of this 2,665,000 tons were obtained from pyrites.

27,500 „ from copper sulphide ores.

285,000 „ „ zinc blende.

and only 25,000 „ „ brimstone.

The following tables (*Soc. Chem. Ind. Ann. Rept.* 1922) are of interest:—

Year	Acid made 100 p.c. tons	Percentage made from			
		Pyrites	Spent oxide	Sul- phur	Zinc and copper fumes
1914	1,082,000	88.9	10.6	0.3	0.15
1917	1,382,000	80.6	11.0	8.1	0.30
1918	1,130,000	81.0	11.2	7.4	0.40

The increase in the consumption of sulphur was mainly due to the operation of Grillo plants designed to burn sulphur only.

Raw materials used in Great Britain and Ireland for acid manufacture (tons).

Year	Pyrites	Spent oxide	Sulphur
1919	588,000	112,000	6,700
1920	686,000	139,000	5,000
1921	313,000	103,000	8,000
1922	391,000	157,000	30,000
1923 (estim.)	348,000	145,000	66,000

The annual consumption of sulphuric acid in England previous to the year 1914 was about 1,040,000 tons (as 100 p.c.), and in addition to this 22,000 tons of Oleum (also as 100 p.c. acid). A production of 1,265,000 tons and 450,000 tons respectively is computed as possible with the increased plants available (*see also J. Soc. Chem. Ind.* 1921, 246 R; 1922, 177 R).

Full statistics relating to the world's production and consumption of pyrites and sulphur are given in a publication of the Imperial Mineral Resources Bureau. H. A. A.

SULVANITE. Sulpho-vanadate of copper, $3\text{Cu}_2\text{S}, \text{V}_2\text{S}_5$, containing vanadium 13.9 p.c. The massive mineral is bronze-yellow with metallic lustre; sp.gr. 4.0, $H.=3\frac{1}{2}$. It shows indications of a cleavage and is no doubt isomorphous with enargite ($3\text{Cu}_2\text{S}, \text{As}_2\text{S}_5$). It is found in considerable quantity with copper-ores, vanadium-ochre, &c., in a mine near Burra in South Australia. L. J. S.

SUMACH. True sumach consists of the dried and usually powdered leaves of the genus *Rhus* (order *Terebinthaceæ*), and is useful for tanning the finer kinds of leather, and also in dyeing and calico-printing on account of the tannin matter present in it.

Sicilian sumach, the variety most esteemed in this country and throughout Europe, consists of the leaves of the *Rhus Coriaria* (Linn.), a shrubby bush cultivated to a large extent in Sicily, where the sumach industry is of considerable importance. When the plant is about to flower the younger twigs are removed, dried in the sun, and subsequently beaten to remove

the leaves and flower panicles. The sumach is imported sometimes in leaves, but more often in the form of powder, and should contain about 25 p.c. of tannin, although as much as from 27 to 32 p.c. may occasionally be found.

According to Löwe (Zeitsch. anal. Chem. 12, 128), the tannin matter present $C_{14}H_{10}O_9$, is ordinary gallotannin; indeed, it is well known that when an aqueous extract of the sumach is boiled with dilute sulphuric acid, considerable quantities of gallic acid are produced. On the other hand, Strauss and Geschwender (Zeitsch. angew. Chem. 1906, 1121), who isolated the tannin according to Löwe's instructions, detected the presence of a methoxyl group, and suggest the formula $C_{32}H_{29}O_{11} \cdot OMe$.

Sicilian sumach contains also a trace of an ellagitannin and myricetin, $C_{15}H_{10}O_8$, to the extent of about 0.1173 p.c. (Perkin and Allen, Chem. Soc. Trans. 1896, 69, 1299), the latter colouring matter having been previously mistaken by Löwe (Zeitsch. anal. Chem. 1874, 12, 127) for quercetin.

Considerable quantities of sand and sometimes particles of magnetic iron ore, which cause black stains, are often to be found in sumach (Procter, Principles of Leather Manufacture, 1903, 271; compare also Trotman, J. Soc. Chem. Ind. 1904); and it is frequently highly adulterated in the ground condition with the leaves and twigs of various plants. Of these, the *Pistacia Lentiscus* (Linn.) ('schinia' or 'skeñs'), *Coriaria myrtifolia* (Linn.) (French sumach or 'stinco'), *Tamarix africana* (Poir.) (brusca), *Tamarix gallica* (Linn.), *Ailanthus glandulosa* (Desf.), *Ficus Carica* (Linn.), *Vitis vinifera* (Linn.), other species of the Rhus family, and also the ground branches ('gambuzza,' 'gammuzza') of the *R. coriaria* itself are known to be employed. These sumach adulterants also contain tannin matters, but for tanning and dyeing purposes are as a rule much inferior to sumach itself.

The *Pistacia Lentiscus* (Linn.) (mastic tree), a small tree about 20 ft. high with evergreen leaves, grows abundantly in Cyprus. The leaves of this plant constitute the most important sumach adulterant, and about 10,000 tons are said to be exported from Tunis to Sicily annually and re-exported thence (as sumach?). According to Procter (*l.c.*) the leaves contain 12–19 p.c. of a catechol tannin. A good plump leather can be obtained from this material, but of a faintly reddish tint, the result being intermediate in character between those which are given by oak bark and sumach. Its presence in sumach is to be deprecated, and in many cases leads to injurious results. A considerable quantity, however, is consumed at Lyons in France as an assistant dyeing material for silk stuffs.

According to Perkin and Wood (Chem. Soc. Trans. 1898, 73, 374), these leaves contain a tannin closely allied to, if not identical with, ordinary gallotannic acid, as when an aqueous extract is boiled with dilute sulphuric acid a considerable quantity of gallic acid is produced. A second tannin or tannin glucoside is also present which, although possessing the general characteristics of the so-called 'catechol' tannins in that it yields a red phlobophane, and as noted by Procter, a reddish coloured leather, gives, by fusion with alkali, gallic acid and phloroglucinol.

In addition to these tannins, myricetin

(probably as glucoside) $C_{15}H_{10}O_8$ is also present to the extent of about 0.15 p.c.

Tamarix africana (Poir.) is a small shrub or tree characterised by its twiggy branches and minute scale-like leaves. The small twigs are collected in Tunis and imported into Sicily for the adulteration of sumach (Procter).

According to Perkin and Wood (*l.c.*), the leaves contain a tannin probably identical with gallotannin, in addition to a small quantity of an ellagitannin. A trace of yellow colouring matter is also present and consists of a quercetin-methylether $C_{16}H_{12}O_7$.

The *Tamarix gallica* (Linn.) closely resembles in appearance the *T. africana* and flourishes in Cyprus, where the latter is not found. According to Procter, it contains 8.4 p.c. of tannin matter.

Ailanthus glandulosa (Desf.) is a tree of large size and handsome appearance, native of India and China but common on the Continent. The leaves contain 11.2 p.c. of tannin matter (Procter) and this resembles gallotannin, although a trace of an ellagitannin is also present (Perkin and Wood). Curiously enough, although it contains so high a percentage of tannin, leather is scarcely tanned by an extract of these leaves, but is merely stained a dull dirty colour. This material is therefore of little use for tanning purposes, and as an adulterant of sumach exerts a deleterious influence. A small quantity of quercetin can be isolated from the leaves.

The leaves of the *Ficus carica* (Linn.) (common fig tree) contain 1.6 p.c. of tannin (Procter) and a trace of a yellow colouring matter (Perkin and Wood). Skin is untanned by an extract of these leaves, but acquires, during the process, a dirty olive tint.

Gambuzza consists of the small stalks branching from the main root of the *R. Coriaria* (Linn.) which are ground to powder and mixed with sumach. The material contains some quantity of a tannin resembling gallotannin, together with a trace of myricetin.

Attempts to detect the presence of these adulterants in sumach by chemical methods have not given satisfactory results, but should a prolonged boiling of the extract with dilute sulphuric acid cause the gradual precipitation of phlobophane, the presence of the leaves of the *Pistacia lentiscus* may be suspected.

Microscopical examination is preferable, and an elaborate work on this subject has been carried out by Andreasch (Sicilianischer Sumach und seiner Verfälschung, Wien, 1898); the book, however, is unsuitable for abstraction. A useful method, now genuinely adopted by leather trades chemists, has been devised by Lamb and Harrison (J. Soc. Dyers, 1899, 14, 60), and is based upon the behaviour of the leaf mixture with warm nitric acid. Under such treatment, the more delicate leaf structure of sumach itself is completely destroyed, whereas the strong cuticles of *Pistachia lentiscus*, *Coriaria myrtifolia*, *Tamarix africana* and *Ailanthus glandulosa* are unaffected and can then be readily recognised (compare also Lamb, *ibid.* 1904, 20, 265). Again, the leaves of the *R. coriaria* are very easily distinguished from those of other plants employed for their adulteration in that both upper and lower cuticles are covered with a dense growth of hairs (Priestman, J. Soc. Chem. Ind. 1905, 24, 231).

Venetian sumach or *Turkish sumach* consists of the leaves of the *Rhus Cotinus* (Linn.), a small tree the wood of which constitutes the yellow dyestuff known as 'Young Fustic.' The material contains about 17 p.c. of tannin, which resembles ordinary gallotannin, together with a trace of an ellagitannin. The presence of myricetin $C_{15}H_4O_2(OH)_6$ in these leaves is interesting, in view of the fact that in the wood itself, fisetin $C_{15}H_6O_2(OH)_4$ is present (Perkin, Chem. Soc. Trans. 1898, 73, 1016).

American sumach.—The leaves of numerous varieties of *Rhus* are employed in the United States for tanning and dyeing purposes, and of these the *R. glabra* (Linn.) very largely takes the place of Sicilian sumach. It contains about 25 p.c. of a tannin closely resembling gallotannin, but produces a leather of very much darker colour than the Sicilian product.

Of the other varieties, *R. typhina* (Linn.) or 'Virginian sumach' (10–18 p.c.), *R. cotinoides* (Nutt.) (21 p.c.), *R. semialata* (Murr.) (5 p.c.), *R. aromatica* (Ait.) (13 p.c.) (Procter), *R. Metopium* (Linn.) (about 8.2 p.c. of tannin, probably gallotannin, together with traces of both quercetin and myricetin) (Perkin, Chem. Soc. Trans. 1900, 77, 427), *R. copallina* (Linn.), *R. pumila* (Michx.), and *R. Toxicodendron* (Linn.) are to be found in the States. Among these, *R. glabra* and *R. copallina* are considered to be worthy of extended cultivation.

In India, numerous species of the genus *Rhus* are known to exist (Watt's Dictionary, Economic Products of India), and again in Algeria the *R. pentaphylla* (Desf.) is used by the Arabs for tanning goat-skins. Finally, the *Anaphrenium argenteum* (E. Mey.) (*R. Thunbergii*) (Cape of Good Hope), 28 p.c. of tannin (bark), probably of the catechol class (Procter), and the *Rhodosphaera rhodanthema* (Engl.) (*Rhus rhodanthema*) (New South Wales), 9.5 p.c. of tannin (leaves), resembling gallotannin, are worthy of mention. The latter plant, also known as the 'yellow cedar,' closely resembles the *R. cotinus*, and it is interesting to note that although the wood of this tree contains fisetin $C_{15}H_4O_2(OH)_4$, the colouring matter of the leaves is quercetin $C_{15}H_3O_2(OH)_5$ (Perkin, Chem. Soc. Trans. 1898, 73, 1017).

French sumach is derived from the *Coriaria myrtifolia* (Linn.), a low deciduous shrub, native of Southern Europe, and has been referred to above as an adulterant of Sicilian sumach. In addition to tannin (15.6 p.c., Procter), which consists probably of ordinary gallotannin together with a little ellagitannin, it contains the poisonous glucoside *coriamyrtin* (Riban, Chem. Zeit. 1867, 663) and a trace of quercetin (Perkin, Chem. Soc. Trans. 1900, 77, 428). According to Procter, the colour of leather tanned by these leaves is very satisfactory and practically equal to that produced by genuine sumach (*R. coriaria*). It is also employed in black dyeing.

Cape sumach consists of the leaves of the *Colpoon compressum* (Berg.) (*Osyris compressa*, *Fusanus compressus*, *Thesium colpoon*), and is much used in South Africa under the name of 'Pruimbast.' The bush is found in the mountains, where it grows to the height of about 6 ft., and only the younger leaves are gathered. These leaves contain about 23 p.c.

of tannin (Procter) which has been isolated as a hygroscopic transparent glassy mass and is probably a catechol tannin glucoside. With boiling dilute acid, a reddish-brown phlobophane is gradually separated, and on fusion with alkali protocatechuic acid is produced (Perkin, Chem. Soc. Trans. 1897, 71, 1135). In addition to tannin there is also present a considerable quantity of the quercetin glucoside *Rutin* (*Osyritrin*) (Chem. Soc. Trans. 1910, 98, 1776). According to Procter, this material forms a useful substitute for Sicilian sumach.

In lieu of the *Colpoon compressum*, a tanning agent known as 'broach leaves' (botanical origin lacking) appears to be considerably employed in South Africa. It contains about 19.9 p.c. of tannin of the so-called 'catechol' variety, together with traces of both quercetin and myricetin (Chem. Soc. Trans. 1898, 73, 384).

Russian sumach consists of the leaves of the *Arctostaphylos Uva-ursi* (Spreng.) (Bearberry), and is said to contain about 14 p.c. of tannin, which, according to Perkin (Chem. Soc. Trans. 1900, 77, 424), consists of a gallotannin together with traces of an ellagitannin. Minute amounts of both quercetin and myricetin have been isolated from this material.

Considerable quantities of 'sumach extract' are now manufactured for dyeing and tanning purposes from genuine Sicilian sumach, and this is usually found on the market as a brown treacly liquid of about 52°Tw. So-called *decolorised* extracts are also prepared to compete with ordinary tannic acid, and for this purpose the addition of blood albumen to the dilute extract at about 48°, then raising the temperature to 70°, and subsequently filter-pressing, gives the most satisfactory results. Sulphurous acid again is employed to brighten the colour of extracts and acts partly as a weak acid in decomposing the inorganic salts of the tannin or colouring matter and partly as a reducing agent. In this case it is usual to pass sulphur dioxide through the liquor before concentration (Procter). A. G. P.

SUMACH WAX *v.* *Japan Wax*, art. WAXES.

SUMATRA WAX *v.* *Fig-tree Wax*, art. WAXES.

SUNFLOWER, *Helianthus annuus* (Linn.). A Mexican plant, now grown in many warm countries for the oil contained in its seeds. The seeds, which differ greatly in size, according to the variety (3000 to 6000 seeds weighing 1 lb.), consist of a hard woody envelope and an oily kernel.

Average composition of the seeds (König):—

	Water	Pro- tein	Fat	N-free extract	Fibre	Ash
Whole seed	8.6	13.7	31.3	18.0	25.4	3.0
Kernels	6.7	26.3	44.3	16.4	2.8	3.5

According to Wiley (Bull. 60, 1901, U.S. Dept. of Agric., Div. of Chem.), the following represents the average composition of the products of American-grown sunflowers:—

	Water	Protein	Fat	N-free extract	Crude fibre	Ash
Seeds	4.4	15.0	27.1	20.9	29.2	3.4
Seed shells	6.2	3.0	1.7	23.2	63.8	2.2
Kernels	4.9	26.9	45.2	16.1	2.7	4.3

The sunflower-seed oil from South-eastern Missouri, examined by Jamieson and Baughman

(J. Amer. Chem. Soc. 1922, 44, 2952), had the following characteristics: d_{25}^{25} 0.9193; n_{20}^{20} 1.4736; iodine number (Hanus), 130.8; sapon. number, 188.0; acid number, 2.3; acetyl number, 14.5; Reichert-Meissl number, 0.27; Polenske number, 0.25; unsapon. matter, 1.20 p.c.; sat. acids, 7.1 p.c.; unsat. acids, 86.6 p.c. Detailed analysis: glycerides of oleic acid, 33.4 p.c.; of linolic acid, 57.5 p.c.; of palmitic acid, 3.5 p.c.; of stearic acid, 2.9 p.c.; of arachidic acid, 0.6 p.c.; of lignoceric acid, 0.4 p.c.; and 1.2 p.c. unsapon. matter. Total, 99.5 p.c.

Hungarian-grown sunflowers apparently yield more oil; Windisch (Landw. Versuchs-Stat. 1902, 57, 305) found the following:—

	Water	Protein	Fat	N-free extract	Crude fibre	Ash
Whole seeds	6.9	15.2	28.9	17.4	28.5	3.2
Husks	10.1	6.9	7.9	20.8	51.6	2.7
Kernels	4.0	24.9	50.4	12.8	3.1	4.0

The principal proteid occurring in the seed is edestin (Osborne and Campbell, J. Amer. Chem. Soc. 1896, 18, 609; 1897, 19, 487) associated with heliantho-tannic acid. The edestin from sunflower seeds has the composition: C, 51.54 p.c.; H, 6.99 p.c.; N, 18.58 p.c.; S, 1.00 p.c.; O, 21.71 p.c.

Sunflowers are largely grown in Russia, the seeds being used to some extent as human food in cold weather, as food for poultry and cattle, but chiefly as a source of oil (*v.* OILS, FIXED, AND FATS). The leaves are sometimes used as food for farm animals, being often dried, powdered and mixed with meal for cattle. The stalks are used as manure, being rich in potash and lime, or sometimes, as fuel.

The plant requires much sunshine and prefers rich, dark soil. Excessive nitrogenous manuring is to be avoided, or the growth of stems and leaves is favoured at the expense of the seeds. About a ton of seeds per acre is the average yield in Europe.

The cake left after the expression of the oil from the seeds forms a valuable food for cattle. Kellner gives as its average composition—

Water	Protein	Fat	N-free extract	Crude fibre	Ash
9.2	39.4	12.6	20.7	11.8	6.3

32.4 of the total 39.4 is digestible protein.

If the seeds are not husked or decorticated before the oil is expressed, the resulting cake is richer in crude fibre (up to 30 p.c.) and correspondingly poorer in albuminoids and fat.

The ash of sunflower seeds and of other parts of the plant was examined by American investigators (Wiley, Bull. 60, 1901, U.S. Dept. of Agric., Div. of Chem.), who found it to contain—

	K ₂ O	Na ₂ O	CaO	MgO	Fe ₂ O ₃	P ₂ O ₅	SO ₃	SiO ₂	Cl
Whole seeds	29.0	1.1	9.4	17.9	0.5	38.4	2.9	0.4	0.5
Stems	38.9	3.8	24.1	19.9	1.2	1.5	3.5	1.3	7.3
Leaves	8.0	0.9	44.0	21.5	2.8	3.3	4.5	13.8	1.5
Kernels of seed	25.5	0.8	6.6	14.7	0.4	50.8	1.0	0.2	0.0
Shells of seed	47.4	1.0	20.9	15.9	1.1	6.8	5.0	0.8	1.5
Husks of seed	55.7	1.7	20.1	9.5	0.9	3.7	2.9	2.0	4.6

Sunflowers are therefore an exhausting crop, making great demands on the nitrogen, potash, and phosphoric acid of the soil. H. I.

SUNSTONE *v.* FELSPAR.

SUPEROL. Trade name for *o*-hydroxy-quinoline sulphate.

SUPERPALITE. Trade name for trichloromethyl chloroformate obtained by treating methyl alcohol with phosgene and chlorinating the methyl chloroformate in sunshine. V. Hood and Murdock, J. Phys. Chem. 1919, 23, 498.

SUPERPHOSPHATES *v.* FERTILISERS.

SUPRARENIN, SUPRARENAL GLAND *v.* ADRENALINE.

SURFACE TENSION OF CERTAIN SOLUTIONS. According to Davis, Salisbury, and Harvey (Indust. and Engin. Chem. Feb. 1924, 16, 161), the surface tension of gelatin solutions is investigated by means of the Morgan drop-weight method. Increasing concentration causes decrease in the drop weight. The drop weight rises to a maximum with increasing temperature, and then falls until the transition temperature 38° is reached, when it remains constant. With increasing pH values, the drop weight tends to reach a maximum at 38° for all concentrations. If the solution is first heated to above the transition temperature, determinations may be made up to about 10 p.c. gelatin. The drop weight diminishes slowly with the age of the solutions (Sci. Abstr. 1924, 27, 467). For the measurement of surface tension with very small volumes of liquid and the surface tension of octanes and xylenes at several temperatures, see Richards, Speyers and Carver (Amer. Chem. Soc. J., May, 1924, 46, p. 1196; Sci. Abstr. 1924, 27, 697; Chem. Soc. Abstr. 1924, ii. 661).

The stability of a solution of hydrogen peroxide in water is decreased by the addition of substances which raise the surface tension of the mixture, whilst by the addition of a substance which lowers the surface tension, the initial titre of the solution remains almost unaltered for a considerable time. There appears to be no quantitative relation between the decrease in stability and the increase in surface tension due to the addition of small quantities of different substances ((Mme.) A. Lisievici-Drăganescu, Bull. Soc. chim. România, 1924, 6, 42; Chem. Soc. Abstr. 1924, 126, ii. 404).

SYENITE. A plutonic igneous rock consisting typically of a coarse-grained crystalline aggregate of potash-felspar (orthoclase) and hornblende. Augite or biotite may take the place of hornblende, giving the varieties augite-syenite and mica-syenite. In structure and mode of occurrence syenite is thus similar to granite, differing from it in the absence of conspicuous quartz and in the correspondingly lower silica percentage. With the presence of quartz, syenite grades into hornblende-granite. The original syenite of Pliny, from the Syene quarries at Assuan on the Nile contains quartz together with large pink crystals of orthoclase-felspar, and is now classed as a hornblende-biotite-granite. This rock was much worked by the ancient Egyptians and Romans: an example of it is seen in the Cleopatra's Needle on the Thames Embankment in London. The name was transferred by A. G. Werner, in 1788, to a reddish rock of similar appearance, but containing no conspicuous quartz, the rock of Plauen near Dresden being taken as the type, and this is now the typical hornblende-syenite. Although syenites are of much less abundant

occurrence than granites, they are subject to greater variations in composition, and a large number of varieties have been distinguished by special names. A distinction is sometimes made between potash-syenites and soda-syenites; in the latter (including laurvikite and nordmarkite) the felspar is soda-orthoclase or anorthoclase, and the amphiboles and pyroxenes are of the soda-bearing varieties. With increasing alkalis, especially soda, nepheline is developed, and there is a passage to the important group of *nepheline-syenites*. Some of the variations in composition are illustrated by the following analyses:—

I. Hornblende-syenite from Plauen, near Dresden.

II. Hornblende-biotite-granite from Syene quarries, Egypt (the syenite of Pliny).

III. Augite-syenite (Laurvikite) from Laurvik, Norway (also P_2O_5 0.54).

IV. Nordmarkite (quartz-syenite with much pink micropertthite) from Tonsenaas, Christiania, Norway (also MnO 0.23).

V. Nepheline-syenite (Foyaite) from Serra de Monchique, Portugal (also MnO 0.19, P_2O_5 , Cl , SrO , Li_2O traces).

	I.	II.	III.	IV.	V.
SiO_2	59.83	69.95	58.88	64.04	53.71
TiO_2	trace	0.95	—	0.62	1.03
Al_2O_3	16.85	13.32	20.30	17.92	21.82
Fe_2O_3	—	—	3.63	0.96	0.78
FeO	7.01	4.90	2.58	2.08	2.74
CaO	4.43	1.79	3.03	1.00	1.90
MgO	2.61	0.66	0.79	0.59	0.56
K_2O	6.57	3.47	4.50	6.08	7.07
Na_2O	2.44	3.31	5.73	6.67	8.52
H_2O	1.29	1.27	1.01	1.18	2.27
	101.03	99.62	100.99	101.37	100.59
Sp.gr.	2.73	2.73	2.66	2.65	2.59

Syenites find the same applications as granites for building, ornamental, and road stones. They range in sp.gr. from 2.5 to 2.7; porosity about 1.3 p.c.; average crushing strength 1200 tons per sq. ft. (ranging from 730 to 2200). In the stone-trade some other rocks, such as diabase and diorite, are sometimes classed as syenites. The nordmarkite of the Christiania district is much used as a building stone; and the laurvikite of Laurvik and Fredriksvärn in the south of Norway is extensively exported as an ornamental stone. The latter is an augite-syenite of various shades of bluish-grey (distinguished in the trade as 'dark pearl,' 'light pearl,' and 'imperial pearl'), and contains much anorthoclase, which displays a brilliant metallic-coloured reflection. Nepheline-syenites are of importance as being the home of many rare-earth minerals, *e.g.* eudialyte, mosandrite, rinkite, &c. Their potash is in part contained in the nepheline, which is readily decomposed by dilute acids; so that, being of abundant occurrence at certain localities, these rocks could perhaps be used as a source of potash. V. GRANITE. L. J. S.

SYLVANITE. A native telluride of gold and silver, $AuAgTe_4$ (Au, 24.2 p.c.; Ag, 13.3 p.c.; Te, 62.5 p.c.), of importance at certain localities as an ore of gold. It has long been known from Transylvania (hence the name 'sylvanite'), where it occurs on joint surfaces in

porphyry as slender rod-like crystals aggregated, by twinning, into branching forms suggesting a resemblance to written characters (hence the old names 'graphic gold' and 'graphic tellurium,' Ger. *Schrifterz*). The crystals are monoclinic and possess a perfect cleavage in one direction, parallel to the plane of symmetry; this cleavage is of assistance in recognising the mineral. The colour is silver-white with a brilliant metallic lustre, but on exposure to light the crystals become dull; sp.gr. 8.2. It is found at Offenbánya and Nagyág in Transylvania, and at several places in Boulder Co. in Colorado, and Calaveras Co. in California. At Kalgoorlie in Western Australia it is found as large cleavable masses (L. J. Spencer, *Min. Mag.* 1903, 13, 271). L. J. S.

SYLVINITE v. SYLVITE.

SYLVITE or *Sylvine*. Native potassium chloride (KCl). Bromine is sometimes present in small amount (up to 0.26 p.c.). It crystallises as cubes or cubo-octahedra with perfect cubic cleavage, but, as proved by etching experiments, these possess a lower degree of symmetry (plagihedral-cubic) than crystals of rock-salt (halite). The crystals are colourless or sometimes bright blue, and they are indistinguishable in appearance from crystals of rock-salt. The two minerals may, however, be readily distinguished by the colour they impart to the Bunsen-flame, by their sp.gr. (1.99 for sylvite, 2.15 for rock-salt), and refractive index (1.491 and 1.547 respectively for sodium-light). Good crystals are found amongst the abraum-salts at Stassfurt and Leopoldshall in Prussia, and at Kalusz in Galicia. More usually it forms granular masses intimately intermixed with rock-salt and sometimes kieserite ($MgSO_4 \cdot H_2O$); such material being known locally as *sylvinit* or 'Hartsalz.' It occurs as beds a metre or more in thickness above the kainite in the carnallite zone; and has probably been formed by the leaching of the deliquescent carnallite ($KCl \cdot MgCl_2 \cdot 6H_2O$), the magnesium chloride being removed in solution to be re-deposited as bischofite ($MgCl_2 \cdot 6H_2O$) in deeper and drier parts of the deposit. In fact, sylvite is now being formed as a crystalline powder or sometimes as stalactitic and botryoidal masses in the mine galleries penetrating beds containing carnallite. Other localities for sylvite are the southern Harz and Werra districts, Hanover, and Mecklenburg; Wittelsheim in Upper Alsace; Suria in Catalonia, Spain; in small amounts at Berchtesgaden in Bavaria, and Hallein in Salzburg; Stebnik in Galicia; Tîrgu-Ocna in Roumania; the Salt Range in the Punjab, India; in the salt-deposits of Sicily, as well as a volcanic product on Mount Etna; in certain of the nitratine deposits of Tarapaca, and in other saline deposits in Pampa of Tamarugal in Chili, and near Lima in Peru. As a granular incrustation intermingled with sodium chloride and other salts it has long been known on Vesuvian lava, and small cubes were found after the 1903 eruption. The latter are intimately associated with cubes of rock-salt, but without forming mixed crystals. L. J. S.

SYMPHOROL v. SYNTHETIC DRUGS.

SYNCHYSITE v. PARISITE.

SYNGENITE. Hydrated potassium and calcium sulphate, $K_2SO_4 \cdot CaSO_4 \cdot H_2O$, containing K_2O 28.6 p.c., crystallised in the monoclinic

system. The colourless glassy crystals have perfect cleavages and a tabular form; they are sometimes twinned, giving rise to a pseudo-orthorhombic habit. Before the discovery of the natural crystals, the artificial salt had, in fact, been described as orthorhombic. Sp.gr. 2.603; $H.=2\frac{1}{2}$. It is readily decomposed by water with separation of calcium sulphate. The mineral occurs with rock-salt, gypsum, and anhydrite beneath the 'abraum' salts, and has been found at Kalusz in Galicia and Stockhausen in Thuringia.

L. J. S.

SYNTHALIN. Trade name for piperonyl-quinoline carboxylic acid methyl ester.

SYNTHETIC DRUGS or MEDICINAL PRODUCTS. Revised by Professor G. Barger, F.R.S., Professor of Chemistry in Relation to Medicine in the University of Edinburgh.

The employment of synthetic coal-tar products in internal medication may be said to date from the introduction of 'kairin,' a synthetic substitute for quinine, discovered by O. Fischer in 1882. The unsatisfactory results attending the administration of this preparation and the difficulties encountered in synthetic work in this direction, caused a lapse of interest until the accidental discovery of the antipyretic properties of antipyrine in 1885 and acetanilide in 1888. The simplicity of the structure of the latter, with its valuable medicinal properties, attracted the attention of pharmacologists, who tried to determine the source of its physiologic action. For example, it was found that aniline was oxidised in the organism into para-aminophenol. This observation led to the introduction of a number of derivatives of *p*-amino-phenol, among which phenacetin was the most successful and best known. As a result, new and valuable products began to follow in quick succession, attracting the attention of the medical profession and of capitalists, until to-day the preparation of synthetic drugs forms one of the most important branches of the coal-tar industry. From the enormous amount of study on the part of pharmacologists and chemists, many valuable data have been collected bearing on the relation existing between chemical structure and physiological action, so that the medicinal action of certain nuclei may, in a measure, be modified to suit the demands of modern medicine. In tracing such relationships, one is struck by the fact that several entirely different nuclei possess similar medicinal properties, for example, the derivatives of aniline (acetanilide, phenacetin), pyrazolone (antipyrine), hydrazine (pyrodine), quinoline (analgene) and salicylic acid (aspirin). That is, these nuclei become antipyretics when suitable side chains are associated with them; under other conditions they become antiseptics. Although the action of substituting groups is in general influenced by their nuclei, yet certain side chains develop latent activities in one direction and others in another, or they may either harm or destroy medicinal action entirely. While physiologic action may in a general way be dependent on chemical structure, modified by solubility, relative stability in the organism, &c., yet this relationship is, as thus far determined, quite obscure outside of certain generalizations. One should not assume that the relationship between structure and physiological action is such that it may be formulated into

definite laws. Ehrlich held that the selective action of organic medicinal compounds depends on the presence of certain 'anchoring' groups. These may be altered so that they or other groups may anchor to different cell-groups or tissues producing a different physiologic action. These views are parallel with the 'chromophore' theories of Witt. For example, the anchoring group of morphine is probably one of its hydroxyls which attaches the active complex to the nerve tissues of the central nervous system. If this group be sulphonated no anchoring takes place, with a consequent loss in physiologic action; while if the hydroxyl be linked with an alkyl or acid rest (as diacetyl or ethyl morphine), attachment to the respiratory centres takes place.

The groups that favour or develop the physiological action of a nucleus are chiefly the amino, alkyl, hydroxyl, carbonyl, and halogens. If the physiological action of a nucleus be excessively intensified through, for example, an amino group (aniline), this may be controlled through the introduction of an organic acid radicle (as in acetanilide), avoiding carboxylic and sulphonic acid groups which produce weak or inert compounds. For example, poisonous phenol may be converted into the non-toxic phenol sodium sulphonate, or morphine into the inert morphine sulphonic acid, or the toxic methylamine into the harmless glycine NH_2-CH_2-COOH . Of primary importance is the deportment of these organic compounds in the human organism, for no inference, as to the manner in which they may split up, can be drawn from laboratory experiments. For example, of two substances differing but slightly in structure, one readily splits up whilst the other is eliminated unchanged. Readily oxidisable bodies like uric acid and creatinine pass through the organism unaltered, whilst succinic acid, not changed by concentrated nitric acid, is consumed to carbon dioxide and water. Kobert states that the action of a drug is not relative to the extent of its chemic changes in the body, as, for example, some very potent alkaloids pass through the system unchanged while certain inert bodies, as tyrosine and succinic acid, are completely oxidised. Most physiologically active organics show more or less complete chemical changes in the body. Through the enzymes of the intestinal canal as well as of the body fluids, ingested chemicals of this class split up, and their physiological action depends upon the resulting decomposition products. It is upon this fact that the synthetic chemist must base his theories relative to action desired. Sometimes unexpected decomposition takes place in the acid secretions of the stomach and unanticipated effects result; as, for example, malarin, a condensation-product of acetophenone and *p*-phenetidine was theoretically an ideal remedy for migraine, but because of its decomposition in the stomach an unexpected systematic toxic effect from liberated *p*-phenetidine resulted. Many of the modern organic synthetic medicinals possess secondary undesirable or toxic effects, hence it is the aim of the chemist and pharmacologist to so alter the structure of such drugs that they can be placed in the hands of the medical profession and even of the general public. While severe criticisms have been offered on

the secondary effects of synthetic drugs, it must not be forgotten that medical authorities frequently subject them to more severe tests than our older and better known remedies can withstand. Caution must always be exercised with remedies involving idiosyncrasies and cumulative effects. A great stimulus to this search after new remedies has been the success attending the study of the structure (chemical and pharmacological) of the alkaloids, which has resulted in the production of compounds from which the objectionable features of the natural products have been, in many cases, eliminated. For examples we have the many local anæsthetics as cocaine substitutes, as anæsthesine, procaine, and nirvanin; and the codeine succedaneums as heroin and dionin. The study of the structure of caffeine has given us theophylline and its derivatives; the same applied to atoxyl brought out salvarsan and its derivatives; the sedative effects of valerian led to its study and the production of a variety of such compounds as validol, adamon, and zeobromal; the undesirable effects of salicylic acid have given us the aspirin class of derivatives, and so on.

Various methods of classification (chemical and physiological) of the synthetic drugs have been attempted, but none of them is entirely satisfactory. One method classifies the aliphatic derivatives under hypnotics and anæsthetics, and those of the aromatic series under antipyretics and antiseptics; another classification takes up the pharmacology of the various groups, for example, the aliphatic hydroxyls as narcotics, the aromatic phenols as antiseptics, the aromatic amino derivatives as antipyretics, &c. Since the structure and nature of the various nuclei influence largely the pharmacology of these radicles, this method is open to objection. The physiological classification is objectionable to the chemist, since compounds of entirely different structure are arranged under the same heading. In this article the method adopted consists in arranging the compounds into general groups according to their medicinal action; as, for example, antipyretics, hypnotics, antiseptics, &c., the compounds under these groups being classified chemically as far as possible. The object has been to give prominence to the presence of certain nuclei and groupings which occur in each of these classes, and to the influence exerted by the introduction of new radicles or structural changes; in other words, to show, wherever possible, the relationship between chemical constitution and physiological action in comprehensive form. For a more detailed *exposé* of this subject, the following works may be consulted:—

Arends-Keller, *Neue Arzneimittel und Spezialitäten* 6 Aufl., J. Springer, Berlin, 1922 (comprehensive, but of no didactic value); M. Barrowcliff and F. H. Carr, *Organic Medicinal Chemicals*, Baillière, Tindall and Cox, London, 1921 (a valuable book dealing with manufacturing processes); S. Fränkel, *Arzneimittel Synthese*, 5 Aufl., J. Springer, Berlin, 1921 (a standard work; has a numerical list of, chiefly German, patents); P. May, *The Chemistry of Synthetic Drugs*, Longmans, Green & Co., London, 1918; Merck's Semi-Annual Reports; New and Unofficial Remedies, Council of Amer.

Med. Assoc. The following are of older date and less detailed: Francis and Brickdale, *Chemical Basis of Pharmacology*, Arnold, 1905; Brickdale, *Guide to New Remedies*, Wright, 1910; H. Hildebrandt, *Neuere Arzneimittel*; H. Peters, *Die neuesten Arzneimittel*.

L. Spiegel, *Chemical Constitution and Physiologic Action*, Constable, 1915, and Fränkel's *Arzneimittel Synthese* may also be consulted on this subject.

Apart from textbooks on pharmacology by Cushny and by Dixon in English, and by Meyer and Gottlieb in German, attention may be directed to A. Heffter's *Handbuch der experimentellen Pharmakologie*, J. Springer, Berlin, of which vol. i. (1923) and vol. ii. pt. 1 (1920) have so far appeared.

Only the more important of the newer chemicals are given, limiting the list to those bearing copyrighted or specially coined titles. For the extensive list of all possible combinations of medicinal chemicals, the reader is referred to Merck's catalogues. Patent numbers are given wherever obtainable. D. R. P.=German Patent; U.S. Pat.=United States Patent; Eng. Pat.=British Patent; U.S. P.=U.S. Pharmacopœia. The names of the manufacturers of the various remedies are abbreviated.

Aethenstaedt=Aethenstaedt and Redeker, Hemelingen, Germany.

Agfa=Aktiengesellschaft für Anilinfabrikation, Berlin, O.

Barnes Co.=A. C. Barnes Co., Philadelphia, Pa.

Bayer=Farbenfabriken vormals Fr. Bayer und Co., Leverkusen, Germany.

Berlin Lab.=Chem. Lab. Gr. Frankfurter Str. 80, Berlin.

Bibus=Dr. B. Bibus, Vienna, I.

Blaes=J. Blaes Co., Lindau in Baden, Germany.

Boehringer=C. F. Boehringer und Soehne, Waldhof bei Mannheim.

Burroughs=Burroughs, Wellcome and Co., London.

Byk=Dr. H. Byk, Windscheid str. 23, Charlottenburg, Germany.

Charlottenburg=Vereinigte Chem. Fabriken in Charlottenburg, Germany.

Ciba=Gesellschaft für Chemische Industrie, Basel.

Cordes=Cordes, Hermann und Co., Hamburg.

Elb=Max Elb, G. m. b. H. Fabrik, Dresden.

Erdmann=C. Erdmann, Leipzig; Lindemann, Saxony.

Falkenberg=Chem. Fabrik Falkenberg, Gruenau, Berlin.

Feigel=E. Feigel, Lutterbach, Alsace.

Fischer=E. W. Fischer, Boehlitz, Leipzig.

Freund=Freund und Redlich, Berlin.

Fritz=G. und R. Fritz, Petzold und Suess, Vienna.

Fritzsche=Franz Fritzsche Co., Hamburg.

Gans=L. W. Gans, Frankfurt, Germany.

Gehe Co.=Gehe Aktiengesellschaft, Dresden.

Gloess=P. Gloess, Solothurn, Switzerland.

Guestrow=Dr. Hillringhaus and Heilmann, Guestrow, Germany.

Heinemann=Ad. Heinemann, Eberswald, Germany.

Helfenberg=Chem. Fab. Helfenberg, Helfenberg, Dresden.

Hell Co.=G. Hell und Co., Troppau, Germany.

Henning=G. F. Henning, Berlin, S.W. 48.

Heyden=Chem. Fab. von Heyden, Radebeul, Dresden.

Hillringhaus=Dr. Hillringhaus und Heilmann, Fabrik, Guestrow.

Hoechst=Farbwerke vorm. Meister, Lucius und Bruening, Hoechst a. M., Germany.

Hofmann=Dr. Hofmann Nachfolger, Merane, Saxony.

Horowitz=Chem. Institut A. Horowitz, Berlin, N. 24.

Kalle=Kalle und Co., Biebrich on Rhine.

Klopfer=Volmar Klopfer, Leubnitz, Dresden.

Knoll=Knoll und Co., Ludwigshafen on Rhine.

Kohlmeyer=C. K. Kohlmeyer und Co., Berlin, W. 10.

La Roche=F. Hoffmann-La Roche Co., Basel.

La Zyma=La Zyma, Montreux, Switzerland.

Lehmann=Berlin Capsule Fabrik, Lehmann, Berlin.

Leonhardt=Leonhardt Co., Zwickau, Saxony.

Lewinsohn=Chem. Institut Lewinsohn, Berlin, S.W.

Lingner=Chem. Fabrik, Lingner, Dresden, A.

Luedy=Luedy & Co., Burgdorf, Switzerland.

Mallinkrodt (Mkdt.)=Mallinkrodt Chemical Works, St. Louis, U.S.A.

Marquart=Chem. Fabrik Marquart, Beuel on Rhine.

Merck=E. Merck, Darmstadt.

Mulford=A. K. Mulford Co., Philadelphia.

Parke Davis=Parke, Davis and Co., Detroit, Michigan.

Poehl=Prof. v. Poehl und Soehne, St. Petersburg, Russia.

Poulenc=Poulenc Frères, Paris.

Reiherstieg=Chem. Werke, Reiherstieg, Hamburg.

Rhenania=Chem. Fabrik Rhenania, Aachen.

Riedel=J. D. Riedel Akt. Gesellschaft, Berlin, N.

Rump=Rump und Lehnern, Hannover.

Sandoz=Chemische Fabrik vorm. Sandoz und Co., Basel.

Schering=Chem. Fab. auf Aktien vorm. E. Schering, Berlin; Schering and Glatz, New York.

Schimmel=Schimmel und Co., Leipzig.

Schoetensack=Chem. Fab. vormals Schoetensack, Ludwigshafen.

Schroder=A. Schroder, Landwehr Str. 45, Munich.

Schuchardt=Theo. Schuchardt, Goerlitz, Germany.

Schuelke=Schuelke & Mayr, Hamburg.

Schuetz=Dr. Schuetz und v. Cloedt, St. Vith on Rhine.

Schulz=Chem. Fab. Fritz Schulz, Leipzig.

Siegfried=B. Siegfried, Zofingen, Switzerland.

Speier=Dr. Speier und Karger, Berlin, N. 54.

Speyer=Speyer und Grund, Frankfurt on Main.

Trommsdorf=H. Trommsdorf Aachen.

Valentiner=Valentiner und Schwarz, Plagwitz, Leipzig.

Van Gember=Van Gember und Fehlhaber, Weissensee, Berlin.

Voswinkel=Dr. A. Voswinkel, Berlin, W. 57.

Weil=Drs. R. und O. Weil, Frankfurt on Main.

Wolfrum=H. Wolfrum und Co., Augsburg.

Wuelfing=J. A. Wuelfing, Berlin, S.W. 48.

Zimmer=Vereinigte Chininfabriken, Zimmer und Co., Frankfurt on Main.

Hydrocarbons. The aliphatic hydrocarbons, provided they are sufficiently volatile, possess in general a narcotic action, influencing the central nervous system in gradually paralysing in turn the functions of the brain, spinal cord and medulla oblongata, affecting first the sensibilities as regards external impressions and stimulation. The physiological intensity of these narcotics increases with their carbon content and relative volatility. From pentane to octane each member is about three times as active as its lower homologue, and is about one-third as soluble in water (Fühner, *Biochem. Zeitsch.* 1921, 15, 235). Somewhere there must be a maximum, for the non-volatile higher paraffins are inert. The unsaturated hydrocarbons are more active than the saturated compounds of the same carbon content. W. E. Brown and V. E. Henderson claim that ethylene may with advantage replace nitrous oxide for general anæsthesia (*Arch. internat. de Pharmacod. et de Thérap.*, 1923, 28, 257). Branched chains, where a number of alkyl groups are linked with a carbon atom, favour narcotic action. This effect is intensified through the introduction of hydroxyls and also halogens in some instances, while in others it is entirely lost. Thus whilst methane is practically free from narcotic effect, the introduction of chlorine develops this action, the intensity increasing with the number of atoms introduced, reaching a maximum in CCl_4 . The same holds for the higher aliphatic homologues, that is not only an increase in narcotic action, but also in their depressing action on the heart and blood vessels; the degree of toxicity being dependent on the percentage of chlorine present. With the chlorinated fatty acids, the reverse prevails, trichloroacetic acid is practically non-toxic, while the monochloro-acid is poisonous. The bromine substitution products deport themselves like the chlorine derivatives, but are less intense in action owing to lower degree of volatility, whilst the chief iodine derivative (iodoform) is valuable only for local application. The aromatic hydrocarbons, on the other hand, possess but very feeble narcotic properties, their action being chiefly convulsive and paralytic in connection with a well-marked lowering of temperature. Benzene at first is a powerful excitant (*cf.* Fühner, above). Through the influence of substituting groups, their untoward action may be almost entirely eliminated, as exemplified among the antipyretics. The benzene hydrocarbons exhibit a paralysing effect on the motor nerves, brain, and spinal chord. The higher homologues of benzene, according to the number and kind of substituting alkyl groups, possess varying toxic action, methyl- and ethyl-benzene are more toxic whilst methyl-isopropyl-benzene (cymene) is

less so than benzene. In general, relative toxicity decreases with the number of alkyl groups introduced, whilst the positions of the substituting groups bear an important part in physiological action. The effect of halogens in the benzene nucleus or its homologues is to increase their antiseptic action which rises with the molecular weight of the halogens.

Hydroxyl groups. The hydroxyl group develops the hypnotic characters of the hydrocarbons, increasing in intensity from the primary to the secondary and tertiary, and with the length of the unbranched chain. While the odour of the lower alcohols is feeble, that of the higher unsaturated alcohols is frequently marked (linalool). With increase in number of hydroxyls, the narcotic effect and odour are replaced by sweet taste, as in the glycols, glycerol, and mannitol. The potent aldehydes are converted through the introduction of hydroxyls into less potent aldols or inactive aldoses (glucoses). Physiologically, the introduction of the hydroxyl group in the aromatic hydrocarbons develops the property of causing a local caustic and antiseptic action, as seen in the phenols. Benzoic acid, through the introduction of a hydroxyl group, is converted into the valuable antiseptic ortho-hydroxybenzoic (salicylic) acid. In those instances where the hydrogen of the hydroxyl group is replaced by an alkyl as glyceryl ether a hypnotic effect is produced. If an acyl radicle is introduced into an alcohol hydroxyl, the result is the effect of the alcohol (*see Alcohols*). While benzene affects the brain first and then the spinal cord, the action of phenol is restricted to the latter, exciting the motor centres of the spinal cord, the convulsive action diminishing with the number of hydroxyl groups. Intensity in physiological action depends upon the relative position of the substituting groups, thus with dihydroxybenzenes toxic action increases from the para- to meta- and ortho-derivatives.¹ Through introduction of alkyls in phenol, intensity of antiseptic action increases, while its caustic and convulsive effects diminish (guaiacol), although in cases where other substituting groups are present the alkyloxy group introduces hypnotic characters (phenetidine derivatives). In veratrole (dimethyl ether of pyrocatechol) the undesirable secondary effects of guaiacol are absent, also its desirable effects, because of too great stability; hence the presence of one free hydroxyl group is physiologically desirable (as in guaiacol), or if covered by an acid radicle (duotal, benzosol), practically the same effects are attained with a minimum of secondary action. The closing of the hydroxyl causing an alteration to a complete disappearance of the primary medicinal action of a substance may be illustrated among the tannins, benzyloxy-tannin being devoid of astringent properties; less marked yet characteristic are eugenol, anisole, phenetole, pyrogallol methyl ether, resorcinol diethyl ether: compare *Synthetic morphine derivatives*. The alkyl ethers are physiologically hypnotics; this extends to many other compounds containing the ethoxyl group as ethoxycaffeine, phenacetine, &c. The introduction of alkyl groups in the nucleus of phenols increases their antiseptic powers. The

¹ Of the trihydroxybenzenes, phloroglucinol is but slightly toxic and caustic, while pyrogallol is very toxic.

same is true of the halogens but to a greater degree, the effect increasing with the number of halogen atoms; this applies to phenols or their ethers. Compounds containing two phenol groups linked together (as in diphenyl or dihydroxydiphenyl-methane) exhibit intensified antiseptic properties. If, however, the linking groups be $-\text{CO}$ or $-\text{SO}_2$, this action is considerably decreased.

Alkyl groups. The effects of alkylation have been summarised by Schmiedeberg² under the following rules: (1) The introduction of simple alkyl radicles diminishes the toxicity of poisonous groups as exemplified in the nitriles, isonitriles (from HCN), or substituted arsenic acid compounds (atoxyl, salvarsan). Also the specific sedative, narcotic or hypnotic effect of the alkyl group may be diminished or disappear through combination with certain groupings, as exemplified in the primary alkylamines. (2) The physiologic action of alkyl oxide (simple or mixed ethers) is equivalent to that of its components, and they resemble in general their corresponding alcohols. In the case of the esters of those acids which are devoid of specific physiologic action, as acetic ethyl ester, their effect is that of the corresponding alcohols; if, however, the acid possesses a distinctive physiologic action, then the effect of the ester is modified accordingly as, for example, in ethyl nitrite. The effects of the methyl group may be seen in xanthine, which is without tonic action on the heart, dimethylxanthine (theobromine) possesses a slight tonic action, while in trimethylxanthine (caffeine) this is still more marked. The hypnotic effect of the alkyl rests is marked in members of the sulphonal group (*see under Ketones*). The methylation of a hydroxyl group diminishes physiologic activity in ratio to the number of alkyl groups entering; for instance, mono-methyl catechol (guaiacol) is less toxic than catechol, dimethyl catechol (veratrole) is still less toxic. The effect of alkylation is especially noticeable among the hypnotics (*l.c.*), there being a marked difference between the methyl and ethyl groups in their action on the central nervous system. Such differences, in another direction, have been pointed out by Ehrlich in that certain dyes containing the diethyl-amino group ($\text{N}(\text{C}_2\text{H}_5)_2$) stain the nerve fibres, while in the corresponding ones containing the dimethyl-amino group ($\text{N}(\text{CH}_3)_2$) this property is lacking. The introduction of methyl groups into the benzene ring generally lowers therapeutic activity (Ehrlich).

Cyanides. The nitriles induce coma, while the isonitriles produce paralysis of the respiratory centres. Neither of these exhibit the intensely poisonous properties of hydrocyanic acid, since they do not liberate HCN in the system, for this reason cyan-acetic acid and the ferrocyanides are non-toxic, while on the other hand, cyanogen chloride is very poisonous, since it liberates HCN. So, then, the relative toxicity of the organic cyanides depends on the readiness and manner in which they hydrolyse in the system, either with liberation of HCN or other more or less stable non-toxic ions.

Nitro compounds. The introduction of a NO_2 or NO group either in an OH group or the

² Archiv f. Exp. Patholog. und Pharmokologie, 1886, 20, 203.

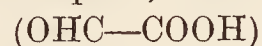
nucleus, cause venous dilation with a consequent decrease in blood pressure—increasing in effect with ascent in the series (example, methyl to amyl nitrite) and the number of nitro groups introduced as in nitroglycerin. The secondary and tertiary nitriles are more active than the primary. The aromatic nitro derivatives of the hydrocarbons are more toxic than their original hydrocarbons, as, for example, nitrobenzene (oil of mirbane) and dinitrotoluene. The nitro acids are usually harmless.

Aldehydes and ketones. Chemic and physiologic reactivity are closely related in the aldehydes, as exemplified in formaldehyde, which is a powerful irritant and tissue hardening antiseptic. The less active acetaldehyde combines the effects of the CHO and CH₃ groups, namely, that of excitation followed by anæsthesia. In the condensation-products as paraldehyde, metaldehyde, chloralamide, aldols, &c., the reactivity of the aldehyde group is repressed through molecular stability. The ketones, like their corresponding alcohols, possess in general, hypnotic properties characteristic of their alkyl groups. Dimethyl ketone (acetone) causes intoxication-hypnosis with accelerated pulse, diethyl ketone and its higher homologues have no such action (*see Ketones under Hypnotics*). Aromatic radicles diminish hypnotic action materially. More profound hypnotics are the ketoximes, in which the duration of sleep increases with the molecular weight of the alkyl group; unfortunately, undesirable secondary effects prevent their use. The influence of the introduction of hydroxyls in the branched carbon chains is the same as with the alcohols, causing complete disappearance of hypnotic action as exemplified in the sugars. The aromatic aldehydes are not usually toxic when their local irritant action is eliminated: this is due to rapid oxidation into their corresponding acids which are quickly eliminated from the system. These bodies play an important part in synthetic perfumery; for example, cinnamic aldehyde, anisic aldehyde, benzaldehyde, phenylacetaldehyde (hyacinth), vanillin, piperonal, citral, &c.

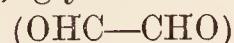
Acids and esters. The introduction of the carboxylic or sulphonic group into compounds of well-defined toxic properties, results in a marked diminution of this action: thus benzene and its derivatives, aniline, naphthalene, phenol, pyridine and quinoline, are far more toxic to the organism than their respective carboxylic derivatives benzoic acid, salicylic acid, naphthalene, pyridine and quinoline carboxylic acids; pyrogallol is far more toxic than gallic acid: the same is true of the corresponding sulphonic acids. Thus symphoral (caffeine sulphonic acid) is purely diuretic; sulphanilic acid and morphine sulphonic acids are inactive.

The first-named poisonous class of aromatic bodies on entering the system, readily submit to oxidation and reduction, giving rise to toxic action, but the relative stability of the carboxyl and sulphonic acid groups and their resistance to processes of oxidation serve to protect the derivatives from further chemical change. Further, the aromatic nitro derivatives lose their toxic effects through introduction of sulphonic or carboxylic groups. Thus the poisonous nitrobenzene and Martius yellow

become the harmless nitrobenzoic acid and naphthol yellow S (dinitro-naphthol sulphonic acid). The lower aliphatic acids seem to accelerate metabolic processes, particularly intestinal peristaltis. Since they are consumed in the body to carbonic acid, their salts serve to increase the alkalinity of the body fluids, hence are of value in gout and similar disturbances resulting from faulty metabolism. The carboxyl group, *per se*, is not toxic but may become so when combined with another atomic complex; thus glyoxylic acid



yields oxalic acid in the urine and is toxic; ethylene glycol which likewise yields oxalic acid yet is non-toxic; glyoxal



which is eliminated unchanged, is very toxic; oxalic acid occurs in urine after ingestion of large amounts of grape sugar. The toxicity of oxalic acid diminishes quickly if methylene groups are inserted between the two carboxyls as in malonic and succinic acids. For further influence of carboxylic groups, see under *Antipyretics*, also *Local Anæsthetics*.

The esterification of the carboxyl group changes it physically and physiologically, usually restoring the original physiologic action of the nucleus or developing narcotic action in the case of the aliphatic acids. Among these products we find many odorous principles such as the 'fruit essences,' also innumerable synthetic perfumes which also possess a distinct narcotic action, moreover such sedatives as validol and bornyval belong to this class. Particularly odoriferous are the esters of the aromatic acids, as methyl salicylate, anthranilic methyl ester, benzyl benzoate, &c. In addition, these esters play an important part in the development of local anæsthetic action in cocaine, eucaine, orthoform, &c. (*see Local anæsthetics*). Since the acid group is usually physiologically inert, the choice of acid for acylation governs the relative stability and consequent rapidity of action of the resulting derivatives. Thus the benzoyl derivatives hydrolyse so slowly in the system that little effect is produced while the lactyl and acetyl compounds hydrolyse rapidly producing prompt medicinal effect.

Organic ammonia derivatives. *Aliphatic amines.* The exciting influence of ammonium hydroxide upon the functions of the spinal cord manifests itself in cessation of breathing, convulsion, and finally paralysis of these centres. The intensity of this action is diminished according to the number of alkyl groups introduced (*see Acetylated amines*), increasing, however, with their molecular weight. The number of amino groups introduced influences relative toxicity, thus the introduction of a second amino group in aniline increases its toxicity, for the phenylene-diamines are very poisonous. With the disappearance of the typical characteristics of ammonia through alkylation, we find another distinctive action developed, especially among the quarternary amines, namely the curari effect. While the narcotic characters of the hydrocarbons disappear when combined with ammonia, we find through introduction of acid radicles (acid amides), this effect reappears, feeble in case of the monobasic acids, and increasing in intensity with molecular weight.

This action is intensified through the well-known action of halogens, for example, diethyl-, dipropyl-, and ethyl-propyl-bromacetamide. Notable is the effect of the introduction of alkyl amines (dimethylamine) in antipyrine (pyramidone), which not only intensifies its specific action, but also eliminates largely its secondary effects. Of special significance is carbonic acid, considered as formic acid in which a hydrogen is replaced by OH, this forms two amides, carbamic acid and urea. As may be expected, the alkyl esters of carbamic acid (urethanes) are hypnotics, the intensity of their action increasing with the molecular weight of the alkyl group, any toxic effects being overcome, as is customary, through the introduction of an acetyl radicle in the amino group. The alkylation of urea does not develop any marked hypnotic action until combined with a dibasic acid radicle, as in barbituric acid (veronal, propanal). The aromatic amines possess such marked antipyretic properties that all possible precautions must be taken to modify their excessive and toxic effects, such as acetylation and alkylation (*see Antipyretics*). If one of the amino hydrogens be replaced by an alkyl, the convulsive is replaced by a paralysing effect. If the alkyl enter the nucleus, the effect of the compound is intensified, however if an acid rest enters the nucleus the effect disappears. Thus the toxic antipyretic aniline becomes the inert amino-benzene sulphonic acid.

The basicity imparted by the amino acids is employed in preparing soluble compounds of otherwise insoluble derivatives (as phenocoll).

The pharmacodynamic actions of other groups are discussed under the special divisions.

ANTIPYRETICS, ANTIRHEUMATICS AND ANTINEURALGICS.

Apart from their medicinal value the organic compounds belonging to this class offer many interesting points in tracing the relationship between chemical structure and pharmacodynamic action. That a number of these substances possess antipyretic, antirheumatic and antineuralgic properties in common may be explained by the close relationship of these diseases, that is, they arise from fundamentally infectious, toxic, or auto-toxic conditions. The majority of the enumerated preparations are derivatives of nuclei possessing a decided toxic action, but by a careful study of the influence of groupings, elimination products and pharmacological structure, primary and secondary toxic effects are more or less eliminated. These latter form the chief difficulties encountered to-day in the preparation of synthetic drugs, for not only must individual idiosyncrasies be considered, but also prolonged medication and possible cumulative effects. Unforeseen difficulties may arise in that a product, which from a chemico-pharmacologic standpoint is ideal, may either undergo a too rapid decomposition or an unanticipated splitting up, or prove to be too stable in the human organism, and thereby fail to accomplish its purpose. With this class of remedies, it is desirable, from a pharmaceutical standpoint, to present them in a soluble form.

Very few are soluble in water. Attempts to render them soluble through sulphonating or carboxylating usually result in comparatively inert products. The use of amino-acids has not proved successful commercially. One of the best examples of this is phenacetin. A consideration of the many derivatives of *p*-phenetidine serves to show the futility of such attempts. The various groups of antipyretics owe their action to essentially different nuclei, but the general principles governing the action of the side chains remain the same. They may be classed as follows:—

I. Acetylated amines.¹ With the introduction of alkyl groups into the ammonia molecule, the convulsive action of the latter materially decreases whilst the narcotic effect of the alkyl disappears in a measure, both components neutralising one another. Quite different is the result of the introduction of the convulsive excitant aromatic alkyls: aniline (phenylamine) influences chiefly the motor centres of the mid-brain (mesocephalon), producing paralysis of its functions, resulting in vertigo, sleep, and finally collapse. Further, aniline and its homologues destroy the hæmoglobin. Apart from these undesirable symptoms, the aromatic amines produce a marked lowering of the temperature, hence are of value in combating fevers, provided the toxic effects can be sufficiently eliminated. The higher homologues of aniline possess like toxic properties, modified, however, by the position of the substituting group; thus metatoluidine behaves like aniline, whilst the ortho- and paratoluidines are much milder. With an alkyl group, as in benzylamine ($C_6H_5 \cdot CH_2 \cdot NH_2$), the antipyretic action almost disappears. To eliminate, as far as possible, the accompanying toxic symptoms of the substituted aromatic amines, we usually resort to the introduction of acid radicles, the substitution taking place in the amino group. As a result of the acetylation of the aromatic amines, more stable and less toxic bodies are produced which are far more resistant to the influences of the circulation. The relative degree of stability increases with the molecular weight of the substituting acid: thus formanilide is more toxic than acetanilide, because of its ready decomposition, while benzanilide and salicylanilide are but mildly antipyretic, since they are less readily split up in the intestine; valerylanilide is inert, being eliminated unchanged from the system. The effect of these anilides are those of aniline, protracted, depending on the relative slowness of their decomposition. If a hydrogen of the methyl group in acetanilide is replaced by COOH, an insoluble, inert, malonanilic acid results. The introduction of a hydroxyl group in the methyl of acetanilide (hydroxyacetanilide), results in no material change in therapeutic effect. The introduction of a sulphonic acid group in the acetyl group (sulphoacetanilide) or the nucleus (acetyl-sulphanilic acid, cosaprin), while giving a more soluble product, results, as previously stated, in greatly diminished potency. If the acetanilide nitrogen be methylated (exalgin $C_6H_5 \cdot N(CH_3)CO \cdot CH_3$), a diminished antipyretic and marked toxic action results. The reverse

¹ Zentralblatt für klin. Med. 1886; Ber. klin. W. 1887, 1, 2.

is the case if the alkyl enters the acid group as in phenylurethane

(euphorin $C_6H_5NH \cdot CO \cdot OC_2H_5$)

which is far less toxic than aniline, and has well-defined analgesic properties, but is irregular in antipyretic action. The popularity of acetanilide may be ascribed more to its use in combination with an alkali bicarbonate with or without caffeine, sold extensively as 'headache powders.' Toluidine derivatives do not offer any advantage over acetanilide.

Acetanilide. Antifebrin

$C_6H_5NH \cdot COCH_3$ m.p. 115° .

Benzanilide (obsolete)

$C_6H_5NH \cdot COC_6H_5$ m.p. 160° – 162° .

Cosaprin. Acet-*p*-sulphanilate of sodium (obsolete)

$C_6H_4(NH \cdot COCH_3)SO_3Na[1 : 4]$

Exalgin. Methyl-acetanilide

$C_6H_5 \cdot N(CH_3)CO \cdot CH_3$ m.p. 101° . Merck.

Methacetin. Acetanisidine

$CH_3O \cdot C_6H_4 \cdot NH \cdot CO \cdot CH_3$ m.p. 127° .

II. Amino-phenols. Phenacetin, the most popular of all antipyretics in medical practice, owes its introduction to the observation that acetanilide undergoes oxidation in the human organism, whereby a hydroxyl group enters the ring in the para- position to the amino group. Thus, *p*-aminophenol¹ was found to be a powerful antipyretic, much less toxic than aniline yet attacking the blood corpuscles with formation of methæmoglobin. The introduction of an acetyl group (acetyl-*p*-amino-phenol) diminished this objectionable feature through greater molecular stability, but not sufficiently until the phenol hydroxyl was covered by an alkyl (ethyl). The chemico-pharmacologic structure of phenacetin is such that as yet no real improvement has been effected. Phenacetin is but slightly toxic when given in very large doses, some methæmoglobin being found in the blood. The methyl derivative (methacetin), possessing a maximum antipyretic effect, has a greater toxic action on the blood, while the introduction of higher alkyls in the hydroxyl group of acetyl-amino-phenol produce weak or inert derivatives owing to excessive stability and failure to split off amino-phenol. The same may be said of aliphatic groups containing COOH (e.g. acetaminophenoxy-acetic acid).

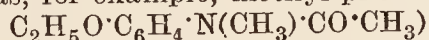
If, on the other hand, an hydroxy acid radicle of the aromatic series replaces the carboxyl hydrogen as in salophen

$HO \cdot C_6H_4 \cdot COOC_6H_4 \cdot NH \cdot CO \cdot CH_3$

salicylic acid and amino-phenol appear in the urine, hence the anticipated antipyretic action. The toxicity of aniline increases through the introduction of an alkyl radicle in the amino group, but diminishes if an aryl radicle is introduced, or there be two alkyl groups.² Further,

¹ Schmiedeberg, Archiv f. exp. Path. u. Phar. 1878, vol. 8, p. 12.

² If the hydrogen of the amino group in *p*-acetamino-phenole be replaced by an alkyl, a narcotic and antineuralgic with low antipyretic action is obtained; as, for example, methyl phenacetin



If an ethyl enters, an increase in narcotic effect with almost undiminished antipyretic action results. In the higher members of the series, as the propyl and butyl derivatives, the narcotic and anti-neuralgic properties rapidly diminish with increase in the molecular weight.

the acid radicle entering the amino group and thus diminishing toxicity must not split off through the action of the gastric secretions, or the undesirable effects of *p*-phenetidine will follow; while, on the other hand, the acid radicle should not be too firmly linked, or an inert product will result. Formylphenetidine, quite unstable, is irritating; while pyrantin (*p*-ethoxy-phenyl-succinimide $(C_2H_5O \cdot C_6H_4 \cdot N(CO)_2 \cdot C_2H_4$ is inert because of excessive stability; the same applies to *iso*-propyl- and *iso*-butyl-phenetidine. Only such derivatives of *p*-phenetidine³ possess an antipyretic action as give the indophenol reaction in the urine, depending on the formation of a red colour upon the addition of nitrous acid followed by beta-naphthol. That is, active derivatives of this class must split up into bodies containing a free amino group (phenetidine or amino-phenol), the intensity of action being in a measure, proportional to the strength of the antipyretic effect or the rapidity of decomposition. The employment of aromatic acids in place of acetic (for the amino group) either diminishes or totally destroys antipyretic action, due to insolubility and failure to break up in the system. The urea derivatives of phenetidine possess antipyretic properties, dulcin (ethoxy-phenyl-carbamide), an intensely sweet chemical, belongs to this group. Attempts to render phenacetin or derivatives of *p*-phenetidine soluble, through sulphonating (*Phesin*) and introducing a carboxyl group (*Benzacetine*)

$C_2H_5O \cdot C_6H_3(NH \cdot CO \cdot CH_3) \cdot COOH$

resulted in excessively stable and medicinally unsuccessful compounds. Phenacetin, the first member of this class to be introduced, is free from serious objection, and has maintained its pre-eminent position. Of the rest, lactophenin and phenocoll have met with success; most of the others have only been used to a small extent.

Amygdophenin. Mandelyl-*p*-phenetidine

$C_2H_5O \cdot C_6H_4 \cdot NH \cdot CO \cdot CH(OH) \cdot C_6H_5$

m.p. 140.5° , Hoechst.

Apolysin. Aconityl-monophenetidine

$C_6H_7O_6 \cdot NH \cdot C_6H_4OC_2H_5$

m.p. 72° (D. R. P. 87428), Heyden.

Brophenin. Bromo-isovaleryl-amino-acet-*p*-phenetidine

$C_2H_5O \cdot C_6H_4 \cdot NH \cdot COCH_2 \cdot NH \cdot CO \cdot CHBr \cdot CH(CH_3)_2$

Citrophen. Monophenetidine citrate. m.p. 188° .

Eupyrine. Carbethoxyvanillylidene *p*-phenetidine

$C_2H_5O \cdot C_6H_4N : CH \cdot C_6H_3(O \cdot CO \cdot OC_2H_5)OCH_3$

m.p. 87° (U.S. Pat. 658446), Zimmer.

Kryofin. Methoxy-acetyl-*p*-phenetidine

$CH_3 \cdot OCH_2 \cdot CO \cdot NH \cdot C_6H_4 \cdot OC_2H_5$

m.p. 98° , Ciba.

Lactophenin. Lactyl-*p*-phenetidine

$C_2H_5O \cdot C_6H_4 \cdot NH \cdot CO \cdot CH(OH)CH_3$

m.p. 118° (U.S. Pat. 503743, expired), Boehringer.

This is less antipyretic and more antineuralgic and narcotic.

Malakin. Salicyl-*p*-phenetidine

$C_2H_5O \cdot C_6H_4 \cdot NH \cdot CO \cdot C_6H_4 \cdot OH + H_2O$

D. R. PP. 79814, 79857; m.p. 92° , Ciba.

³ Hinsberg und Treupel, Archiv f. exp. Path. u. Phar. 1894, vol. 33, p. 216.

- Malarin.* Acetophenone-*p*-phenetidine
 $\text{C}_6\text{H}_5\text{C}(\text{CH}_3):\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{OC}_2\text{H}_5$
 m.p. 88° (D. R. P. 98840), Valentiner.
- Neraltein* (*Nervraltein*). Sodium-*p*-ethoxyphenyl-aminomethane sulphonate
 $\text{C}_2\text{H}_5\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CH}_2\cdot\text{SO}_3\text{Na}$
- Phenacetin.* Acetyl-*p*-phenetidine
 m.p. 134° (U.S. Pat. 400086, expired), Bayer.
- Phenocoll.* Amino-acetyl-*p*-phenetidine hydrochloride
 $\text{C}_2\text{H}_5\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_2\text{NH}_2\cdot\text{HCl}$
 m.p. 95°. Anhydrous base 100·5° (U.S. Pat. 543214, expired), Schering.
- Phenosol.* Salicyloacetate of *p*-phenetidine
 m.p. 182°, Hofmann.
- Phenoval.* Alpha-bromo-*iso*-valeryl-*p*-phenetidine
 $(\text{CH}_3)_2\text{CH}\cdot\text{CHBr}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{OC}_2\text{H}_5$
 m.p. 150° (D. R. P. 277022), Riedel.
- Pyrantin.* *p*-Ethoxy-phenyl-succinimide
 $[\text{CH}_2\cdot\text{CO}]_2\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{OC}_2\text{H}_5$ m.p. 155°, Hoechst.
- Salophen.* *p*-Acetaminophenyl salicylate
 $\text{HO}\cdot\text{C}_6\text{H}_4\cdot\text{COOC}_6\text{H}_4\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_3$
 m.p. 188° (D. R. PP. 62533, 62289; U.S. Pat. expired), Bayer.
- Thermodin.* Phenacetin-urethane
 $\text{C}_2\text{H}_5\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{N}(\text{COOC}_2\text{H}_5)\cdot\text{COCH}_3$
 m.p. 86°–88° (D. R. PP. 69328, 85803), Merck.
- The acetyl derivative has a gradual antipyretic action, is non-toxic, and is without depressing effect on heart or respiration.
- Triphenin.* Propionyl-*p*-phenetidine
 $\text{C}_2\text{H}_5\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{NH}(\text{CO}\cdot\text{CH}_2\cdot\text{CH}_3)$
 m.p. 120° (U.S. Pat. 535846, expired), Merck.
- Valerydin.* Isovaleryl-*p*-phenetidine
 $\text{C}_2\text{H}_5\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CH}(\text{CH}_3)_2$ Erdmann.
- Vinopyrin.* *p*-Phenetidine tartrate
 m.p. 168°, Fischer.

III. Pyrazolone derivatives. These preparations possess antipyretic and analgesic action, with less tendency to disintegrate the red blood corpuscles than the phenetidines. Two erroneous assumptions led to the discovery of this group of antipyretics, namely, that quinine was a tetrahydroquinoline derivative and that what is now known as antipyrine was related to this same ring system. Knorr, in 1884, obtained a condensation-product of phenyl-hydrazine (antipyretic but toxic) and aceto-acetic ester, the resulting phenyl-methyl-pyrazolone, was unsuited for therapeutic purposes. Utilising Filshie's previous experiences with substances of like physiological action derived from quinoline, namely kairine and kairolin, a methyl group was introduced which resulted in the formation of the well-known antipyrine. While this substance does not possess any of the antiperiodic properties of quinine, it has greater antipyretic and antineuralgic effects; in general, its action resembles that of salicylic acid. Phenyl-monomethyl-pyrazolone is only slightly antipyretic. The presence of an aromatic group (like tolyl in tolylpyrine), while not being absolutely essential, increases the efficiency. A great improvement over antipyrine in intensity (3 times), mildness and duration of action was attained through the introduction of a dimethylamino group ($\text{N}(\text{CH}_3)_2$) in place of the

only replaceable hydrogen of the nucleus (pyramidone). The success attending the introduction of pyramidone led to a variety of combinations with camphoric and salicylic acids, &c., none of which offers any material advantages. The Hoechst Co. has patented methyl sulphonates of amino substituted aryl pyrazolone (D. R. PP. 263458, 254711, 259503, 259537, 254487).

Of the substances of this group only antipyrin and pyramidone have attained importance. *Acopyrin* (acetopyrin). Antipyrine acetyl salicylate m.p. 63°/65°, Heyden. *Antipyrin*, Antipyrina, U.S. Pat. Phenyl-dimethyl-pyrazolone $\text{C}_{11}\text{H}_{12}\text{ON}_2$, m.p. 111°–113°.

Ferropyrin $(\text{C}_{11}\text{H}_{12}\text{N}_2\text{O})_3(\text{FeCl}_3)_2$
 (U.S. Pat. 548352, expired), Knoll.

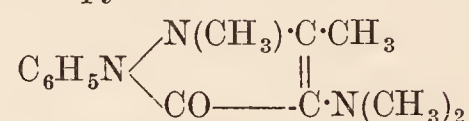
Melubrin. Sodium 1-phenyl-2 : 3-dimethyl-5-pyrazolone-4-aminomethane sulphonate. A pyramidone in which both methyl groups are replaced by the rest of methyl sodium sulphonate.



(U.S. Pat. 1056881), Hoechst.

Phenazonum BP=Antipyrin.

Pyramidone (Amidopyrin, B. P. C.) Dimethyl-amino-antipyrine



m.p. 108° (U.S. Pat. 579412, expired), Hoechst.

Pyramidone neutral camphorate

m.p. 80°–90° (U.S. Pat. 686998), Hoechst.

Pyramidone acid camphorate

m.p. 84°–94° (U.S. Pat. 686999, expired), Hoechst.

Pyramidone salicylate

m.p. 68°–70° (U.S. Pat. 680278), Hoechst.

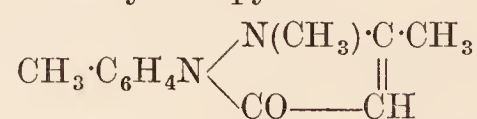
Pyrosal. Acid salicylo-aceto-antipyrine

m.p. 150°, Hofmann.

Salipyrine. Antipyrine salicylate

mp. 92° (U.S. Pat. 444004, expired), Riedel.

Tolypyrine. Toly-antipyrine

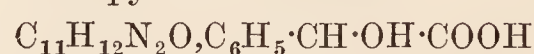


m.p. 137°, Riedel.

Tolysal. Tolypyrine salicylate, m.p. 102°, Riedel.

Trigemin. Dimethylamino-antipyrine butyl chloral hydrate, m.p. 85° (D. R. P. 150799), Hoechst.

Tussol. Antipyrine mandelate



m.p. 53° (U.S. Pat. 569415), Hoechst.

Katamen. Phenyl-dimethyl-sulphamino-pyrazolone benzoate.

Migrol. Pyrocatechin-mono-aceto-dimethyl-amino-phenyl-dimethyl-pyrazolone, Hoechst.

IV. Salicylic acid derivatives (*for internal use*). As is well known, the introduction of a COOH group into compounds of well-defined toxic or antiseptic properties results in a marked diminution of these properties. Particularly is this the case with the phenol acids (salicylic), the ortho-derivative being more toxic and antiseptic than

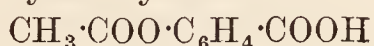
benzoic acid and much less so than phenol, the meta- and para-hydroxy-benzoic acids are inert.

Salicylic acid and its derivatives are far more extensively employed as antipyretics and analgesics than as antiseptics. Because of the size and frequency of the doses and the usual accompanying gastric irritation, which characterises these organic compounds, a large number of insoluble esters and compounds have appeared. Such preparations are intended to pass through the stomach unchanged to the intestinal tract, where they are broken up through the alkaline secretions with liberation of salicylic acid. The liquid (alkyl) esters are more adapted for dermal medication where local effect is desired, however they also serve as a means of medication when the stomach fails to tolerate salicylates.

According to their structure, the salicylic acid derivatives may be classed as follows:—

1. Compounds in which hydrogen of the phenol group has been replaced by acyl radicles. These possess marked analgesic and antipyretic effects, hence are of value in rheumatism, neuralgia, colds, and other conditions where the full physiologic action of salicylic acid is desired.

Aspirin. Acetyl-salicylic acid



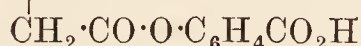
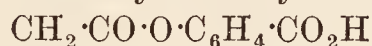
m.p. 135° (U.S. Pat. 644077, expired), Bayer.

The methyl ester of acetyl-salicylic acid is known as *Methyl rhodin*, while the menthol ester is known as *Menthospirin*.

Aspirin soluble. The calcium, sodium, or lithium salts of aspirin. These are readily soluble and claimed to be free from gastric disturbances. Calcium Aspirin or '*Kalmo-pyrin*' or '*Tylcalsin*,' Bayer (D. R. PP. 253924, 255672, 255673; Fr. Pat. 464081). Lithium Aspirin, *Tyllithin* or '*Apyron*,' Wuelfing (D. R. P. 267381). Sodium Aspirin, Wuelfing (D. R. PP. 276668, 270326, 218467). Alkyl halogen esters of Aspirin, Wolffenstein, Berlin (D. R. PP. 258888, 245533, 246383).

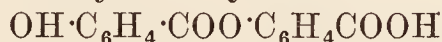
Despyrin. Salicylic tartaric ester.

Diaspirin. Succinyl-disalicylic acid



m.p. 178° (D. R. P. 196634; U.S. Pat. 874929), Bayer.

Diplosal. Salicylo-salicylic acid

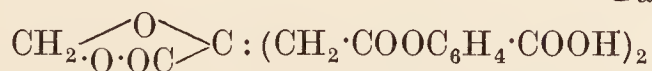


m.p. 147° (U.S. Pat. 922995), Boehringer.

Ervasin is acetyl-p-cresotinic acid.

Novaspirin. Methylene-citro-salicylic acid

(D. R. P. 185800; U.S. Pat. 858142), m.p. 150°, Bayer.



2 (a). Esters in which the H of the carboxyl group is replaced by alkyl groups. Some of this group as benzosalin, salol, salacetol, and glycosal, are used internally exclusively, while the liquid esters mesotan, methyl and ethyl salicylates are used locally.

Algolane. Salicylic ester of propyl-dioxy-isobutyrate. Poulenc.

Ethyl salicylate. $\text{HO}\cdot\text{C}_6\text{H}_4\cdot\text{COOC}_2\text{H}_5$; b.p. 230°–

232°; less irritating and toxic than the methyl ester.

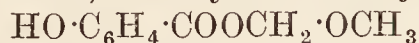
Glycosal. Monosalicylic glyceryl ester



m.p. 71° (D. R. P. 127139), Merck.

Indoform. Salicylic methylene acetate, also stated to be chiefly a mixture of salicylic acid and aspirin, m.p. 108°, Schulz.

Mesotan (erucin). Salicylic methoxymethyl ester



b.p. 162° (42 mm.) (D. R. P. 137585; U.S. Pat. 706018), Bayer.

Methyl salicylate. $\text{HO}\cdot\text{C}_6\text{H}_4\cdot\text{COOCH}_3$, b.p. 224°, for internal use, the natural oils of birch or wintergreen are to be used.

Salibromin. Methyl 3:5-dibromo-6-hydroxy-1-benzoate

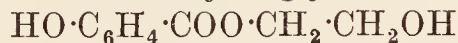


Salacetol. Acetonyl salicylate



m.p. 71°, Schoetensack.

Spirosal. Monosalicylic glycol ester

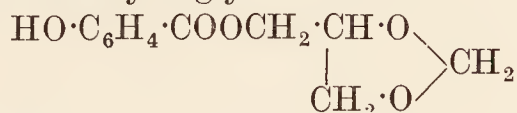


b.p. 170° (12 mm.) (D. R. P. 164128; U.S. Pat. 794982), Bayer.

Alkoxy-alkylidene esters of cresotinic acid are said to excel mesotan (D. R. P. 269335), Bayer.

For external use.—Another method for the employment of salicylic acid, either alone or in conjunction with its internal use, consists in the local application of its various esters. These must be either in fluid form or, if solid, soluble in fats, so that absorption by the skin may readily take place. Owing to the objectionable odour of oil of wintergreen, various other inodorous esters of the aliphatic series have come into use.

Protosal. Salicylic glycerol formal ester



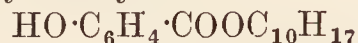
b.p. 200° (12 mm.) (D. R. P. 163518), Schering.

Saligallol. Pyrogallol disalicylate, a resinous substance, at one time recommended for skin affections m.p. 141°, Knoll.

Salimenthol. Menthyl salicylate

(D. R. P. 171453), Bibus.

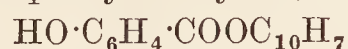
Salit. Bornyl salicylate



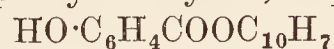
(D. R. P. 175097), Heyden.

2 (b). In this class of esters the hydrogen of the carboxyl is replaced by a phenyl rest. They are of the salol type which contain active phenols and serve as intestinal antiseptics.

Alphol. α -Naphthyl salicylate, m.p. 83°



Betol. β -Naphthyl salicylate, m.p. 95°



Cordol. Tribromosalol



Guaiacol salicylate. Methoxy-salol



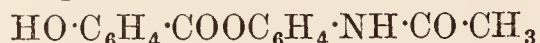
m.p. 65°, Merck

Salicreol. Creosote salicylate.

Salol. Phenyl salicylate



Salophen. *p*-Acetaminophenyl salicylate



m.p. 187°–188°, Bayer. See under *Antipyretics*.

3. Compounds in which both hydrogens of salicylic acid have been substituted.

Benzosalin. Benzoyl-salicylic methyl ester



m.p. 85° (D. R. P. 169247 ; U.S. Pat. 799706),
La Roche.

Menosal. Menthyl-salicylic methyl ester,

Merck.

Methylaspirin. Methyl acetylsalicylate



m.p. 54°, Merck.

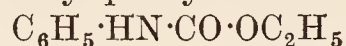
Vesipyrin. Phenyl acetylsalicylate, acetyl-salol



Reiherstieg.

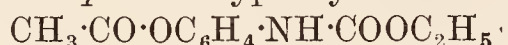
V. Urethane derivatives. It has been noted that the toxic action of aniline or the aminophenols is eliminated by the introduction of carboxyl and alkyl groups in different positions. It has been found that the hypnotic urethanes fulfil these conditions when coupled with a phenyl group, losing, however, their hypnotic characters through change in their structure. These compounds are more especially analgesics (see *Carbonic acid derivatives*).

Euphorine. Ethyl phenylcarbamate



m.p. 50°, Heyden.

Neurodine. *p*-Acetoxypheyl urethane



m.p. 87°, Merck.

Thermodine. Phenacetin urethane



m.p. 86°–88°, Merck.

Cryogenine. *m*-Aminobenzoyl-semicarbazide



(Lumière and Chevrottier, Compt. rend. 135, 187).

HYPNOTICS.

Owing to our lack of knowledge concerning the physiology of sleep and possible chemical processes that take place, we are equally ignorant of the exact manner in which sleep is produced by hypnotics. In effect, we must distinguish between narcotics (represented by opium), which produce unconsciousness by intoxication, and the true hypnotics (represented by chloral), in which the sleep is apparently normal. In view of the fact that the sleep produced by the opium class is often attended with undesirable by-effects, and that during their prolonged administration the element of habituation must always be considered, they have been reserved for cases of insomnia due to severe pain, and have been largely replaced in other forms of sleeplessness by the synthetic hypnotics. While this latter class approach the normal conditions, yet the ideal hypnotic remains to be discovered. This must act upon the nerve centres, followed later by the most automatic and stable centres, avoiding any profound influence on the respiratory or circulatory centres. Elimination must be rapid and

complete, leaving no trace of cumulative or secondary action such as digestive disturbances, headache, &c. The hypnotic effect of the aliphatic hydrocarbons, developed through the introduction of hydroxyl groups (alcohols), is well known. That the hydroxyl serves no further purpose than that of an anchoring group is proved by the inert properties of the polyhydric alcohols. That the ethyl group produces a profound hypnotic effect, as in alcohol, is further demonstrated by the decomposition of chloral in the blood to trichlorethyl alcohol, and the necessary presence of alkyl groups in the most important classes of hypnotics. The introduction of the ethoxyl group into caffeine imparts a narcotic effect. It can be said in general that the alkyl groups, more especially the ethyl, possess a distinct sedative action upon the nervous system. The methyl group generally eliminates or diminishes hypnotic action when associated with an ethyl or propyl group; the propyl radicle with other higher radicles increases the intensity and also toxicity, while their corresponding *iso* groups generally diminish it. Sulphur replacing oxygen contributes to toxicity. The alkyl radicles do not carry hypnotic or sedative action under all conditions; it is only the association of certain groups or nuclei or their structural environment that determines this action. The presence of a sulphonie or carboxyl group inhibits physiological action, and diminishes toxicity. Another factor is insolubility, that is, failure to break down in the system: thus tetronal, which, theoretically, should possess a more profound hypnotic action than trional, is practically inert. A further insight is gained on studying the groups.

Alcohols. As already noted, the ethyl group has a close affinity to the nervous system, serving as a sedative and hypnotic. When this radicle is linked with readily oxidisable groups, the action is very evanescent, hence the hypnotic effect of ethyl alcohol is very slight. If, on the other hand, the combination resists oxidation (as in trional), then the full action of this group manifests itself. Generally speaking, the primary alcohols are less narcotic than the secondary, and these less so than the tertiary. The longer the carbon chain the more potent the alcohol: if more than one hydroxyl is present, narcotic effect disappears in proportion. In tertiary alcohols, the physiological action depends upon the alkyl groups linked to the tertiary carbon, if the methyl radicle be present, as in trimethyl-carbinol (tertiary butyl alcohol), the action is relatively feeble: with ethyl groups, it increases in proportion to the number of such groups united to the tertiary carbon (see *Hydroxyl groups*).

Acetone chloroform = *v*. Chlorbutanol below.

Amylene hydrate $\text{C}_2\text{H}_5\cdot\text{C}(\text{CH}_3)_2\text{OH}$, dimethyl-ethyl-carbinol, b.p. 99°–100°. The introduction of halogens into the hydrocarbons increases hypnotic action, as is shown in methyl chloride and chloroform. A similar effect is attained in:

Antodyne, phenoxy-dihydroxy-propane



m.p. 69°, Poulenc.

Brometone, tertiary-tribromo-butyl alcohol. Parke Davis $\text{CBr}_3\cdot\text{C}(\text{OH})(\text{CH}_3)_2$, m.p. 167°.

Chlorbutanol = Acetone-chloroform or chlore-tone, trichloro-tertiary-butyl alcohol



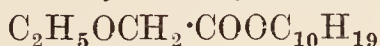
Also used as local anæsthetic, m.p. 96°, Parke Davis.

Isopral, $\text{CCl}_3\cdot\text{CH}(\text{CH}_3)\cdot\text{OH}$, trichloro-isopropyl alcohol (D. R. P. 151545), m.p. 49°, Bayer.

Methaform = Chlorbutanol.

Derivatives of alcohols—

Coryfin, menthyl ethoxyacetate



U.S. Pat. 836914, Bayer.

Methylal (formal). Methylene dimethylether, $\text{CH}_2(\text{OCH}_3)_2$, b.p. 42°.

Valamin, iso-valeric ester of amylene hydrate.

Aldehydes. Acetaldehyde is slightly hypnotic; much more so is its polymeride, paraldehyde. The aldols and acetals (ethylidene diethyl ether) possess a mild effect. The further introduction of alcohol groups, as in sugar, give inert compounds. As cited under the alcohols, the introduction of chlorine or bromine produces a marked increase in hypnotic effect exemplified in chloral, the first synthetic drug. This is converted in the blood into urochloralic acid, a compound of trichlorethyl alcohol and glycuronic acid. The chief objections to the use of this standard hypnotic of the aldehyde group are, that it cannot be used subcutaneously; it is a cardiac and respiratory depressant, and possesses an irritating action on the stomach. To eliminate the secondary irritant action due to the aldehyde group, various combinations have been introduced with partial success in making it safer, but with a reduction in hypnotic action. One of these (chlorbutanol) can be given hypodermically. The corresponding bromine derivatives possess a toxic secondary action, whilst those containing iodine are inert. The following chloral combinations exhibit the same effects as chloral on the heart and respiration without an irritant effect on the stomach since they split up in the intestinal tract.

Chloralamide, $\text{CCl}_3\cdot\text{CH}(\text{OH})\cdot\text{NH}\cdot\text{CHO}$, chloral formamide, m.p. 115° (D. R. P. 50536; U.S. Pat. 429040, expired), Schering.

Chloralimide, $\text{CCl}_3\text{CH:NH}$, m.p. 155°.

Chloralose, $\text{C}_8\text{H}_{11}\text{O}_6\text{Cl}_3$, a condensation product of chloral and anhydrous glucose (Ber. 22, 1051), m.p. 186°–187°.

Dormiol, $\text{CCl}_3\cdot\text{CH}(\text{OH})\cdot\text{O}\cdot\text{C}(\text{CH}_3)_2\text{C}_2\text{H}_5$, dimethyl-ethyl-carbinol-chloral (D. R. P. 99469), Kalle. It is a compound of chloral and amylene hydrate (see above).

Hypnal. Chloral-hydrate-antipyrine, m.p. 67°, Hoechst.

Butylchloral hydrate,



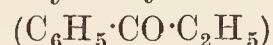
m.p. 78°, prepared by chlorinating paraldehyde.

Butyl-hypnal, Butylchloral-antipyrine, m.p. 70°.

Aromatic aldehydes are usually of low toxicity, since they oxidise to inert acids.

Ketones. The action of these, like the alcohols, is governed by their alkyl groups. Dimethyl ketone produces intoxication, stimulation of heart's action, followed by paralysis of the central nervous system, whilst the diethyl and dipropyl ketones are mild hypnotics, free from

action on the heart. In general, the aromatic ketones are only slightly hypnotic, while the mixed aromatic and aliphatic ketones are markedly so, phenyl ethyl ketone

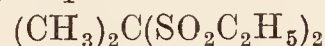


being more powerful than hypnone.

Hypnone $\text{C}_6\text{H}_5\text{CO}\cdot\text{CH}_3$, phenyl methyl ketone, acetophenone, b.p. 198°–200°.

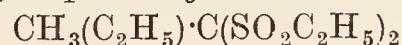
Sulphonal group. This group was first studied medicinally by Baumann and Kast in 1886–1889. Its members, obtained by oxidising the condensation products of ketones and mercaptans, contain the central group $\text{>C}<\begin{smallmatrix} \text{SO}_2\text{—} \\ \text{SO}_2\text{—} \end{smallmatrix}$, which carries the hypnotic radicles in the form of methyl and ethyl groups. Only those disulphones which contain ethyl groups are active, and the intensity of effect depends upon the number of such groups contained in the molecule. This reaches its limit, however, in 'tetronal,' which contains four ethyl groups and because of its insolubility fails to break down in the system, and hence is almost inert. The sulphomethanes produce sleep with no effect on the circulation or respiration. In excessive doses these bodies produce disturbances of the digestive and nervous system, ataxia, albuminuria, and nephritis. Cumulative action may occur, when they are administered for too long periods of time.

Sulphonal, *sulphonmethane*, U.S. P.



diethylsulphone-dimethyl-methane, m.p. 125·6°, pat. expired, Bayer (cf. Ber. 19, 280).

Trional, *sulphonethylmethane*, U.S. P.



diethylsulphone-methyl-ethyl-methane, m.p. 76°, pat. expired, Bayer.

Carbonic acid derivatives. The hypnotics under this heading may be classed as derivatives of carbonic acid, carbamic acid and urea. From carbonic acid, no narcotic action can be expected, since the free carboxyl group is toxic. On the other hand, the esters of carbamic acid (urethanes), have the advantage that so long as the doses are not excessive, important life functions are not disturbed. Any toxic action, as collapse or feeble heart action, may be corrected through the introduction of an acetyl group. Hypnotic action is intensified through increase in size of the alkyl group. Urea is inert when an amino hydrogen is replaced by an alkyl group, the product exhibits the action of the latter. Derivatives with primary alkyls are inert; tertiary butyl-urea is feebly hypnotic; tertiary amyl-urea is stronger, whilst the tertiary heptyl-urea is still more active. If both amino groups are replaced symmetrically by such radicles, medicinal action ceases, owing probably to excessive stability.

Urethane group. The urethanes (carbamic acid esters), once quite popular, have given way to the sulphonal and barbituric acid derivatives. The latter were introduced by Schmiedeberg in 1885. The introduction of an acyl (as $\text{CH}_3\cdot\text{CO}$) into the amino group of urethanes lessens toxicity but does not change their physiologic action.

Urethane $\text{NH}_2\cdot\text{COOC}_2\text{H}_5$, carbamic acid ethyl ester, m.p. 48°–50°. Tertiary alcohol urethanes (D. R. P. 254472). Glycol urethanes

(D. R. PP. 266121, 247270), Voswinkel; and (D. R. P. 269938), Bayer.

Calmonal, double salt of 1 mol. of CaBr_2 with 4 mol. ethyl urethane, m.p. 107° , Gehe.

Hedonal $\text{NH}_2\cdot\text{COO}\cdot\text{CH}(\text{CH}_3)\cdot\text{C}_3\text{H}_7$, see butyl-urethane, m.p. 74° , b.p. 215° (U.S. Pat. 659202, expired; D. R. P. 120865), Bayer.

Aleudrin. The carbamic acid ester of α -dichloroisopropyl alcohol



Aponal, $\text{NH}_2\cdot\text{CO}\cdot\text{O}\cdot\text{C}(\text{CH}_3)_2(\text{C}_2\text{H}_5)$. Amyl carbamate, Zimmer. D. R. P. 245491.

Although hypnotic action is obtained by associating ethyl groups directly with carbon, diethyl-acetic and malonic acids are found to be inert, likewise their corresponding amides. This is due to the failure to replace all replaceable hydrogens of the carbon (in tertiary form). This is demonstrated by introducing a (sedative) bromine into diethyl-acetamide, thus:

Neuronal $(\text{C}_2\text{H}_5)_2\text{C}(\text{Br})\text{CONH}_2$, diethylbromacetamide, m.p. 66° , Kalle. D. R. P. 158220.

The following brominated urea derivatives are important hypnotics:—

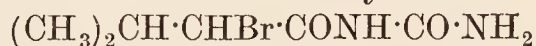
Adalin. Bromodiethylacetyl-urea



m.p. 116° (D. R. P. 225710, Bayer; U.S. Pat. 983425; cf. also Bayer, D. R. PP. 240353, 243233, 249906, 253159, 282097, 286760; Beckmann, D. R. P. 262148).

Adalin is an almost tasteless and odourless sedative and hypnotic, which is recommended for use in cases of neurasthenia and such nervous conditions as are found before minor operations. Its safety is suggested by the fact that while the normal dose as a sedative is one to two tablets of 5 grains each three or four times daily, and as a hypnotic two or three tablets half an hour before bedtime, as much as 125 grains have been taken in a single dose without any undesirable effect other than protracted sleep. As a rule it is well borne by the gastro-intestinal tract, while it does not seem to depress the heart. The tablets can be taken in a little cold water when prescribed as a sedative, and with a hot drink, the nature of which is ordered by the physician, when prescribed as a hypnotic (Lancet, 1924, 206, 1008; Pharm. J. 1924, 113, 46).

Bromural. Bromo-isovaleryl-urea



m.p. 145° (D. R. PP. 185962, 175200; U.S. Pat. 914518), Knoll and Merck.

Malonyl-urea derivatives, $\text{CH}_2\langle\text{CO}\cdot\text{NH}\rangle\text{CO}$

Neither malonic acid nor its amide possesses hypnotic action. The introduction of two methyl groups into the latter is without effect, and one methyl and one ethyl imparts a mild hypnotic action; marked, however, is that produced through the presence of two ethyls, as in:

Veronal, *Barbitonum*, B.P. *Barbital* or *Barbitone*,



diethyl-barbituric acid, diethyl-malonyl-urea, m.p. 188° . This commercially very important hypnotic has been the subject of numerous patents. The chief methods of manufacture are

from ethyl diethylmalonate (D. R. P. 146496), from ethyl diethylcyanoacetate (D. R. PP. 156384, 156385), and from diethylmalonyl chloride, by condensing in each case with urea. For these and numerous other methods of preparation, with list of patents, see Organic Medicinal Chemicals, by Barrowcliff and Carr, pp. 43–47 (U.S. Pat. Bayer, 782739, cancelled; Merck, 258057, 265726). The introduction of the propyl radicle increases the duration of the hypnotic effect, whilst *isobutyl* and *isoamyl* radicles diminish this. A substitution of the imide hydrogens of veronal by alkyls as well as that of oxygen by sulphur yield toxic bodies.

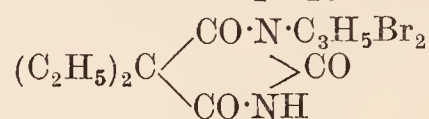
Veronal sodium or *medinal* is of more rapid action because of ready solubility.

A mixture of 2 parts of codeine diethyl-malonylurea with one part of the sodium salt is used as sedative and hypnotic—*Codeonal* (D. R. P. 239323). Knoll.

Veronacetin. Phenacetin-veronal.

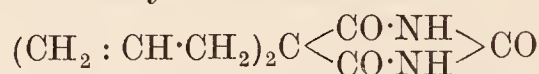
Chineonal. A compound of veronal and quinine which fuses at 132° . Used in infectious fevers, also as an analgesic. Merck.

Diogenal. N-dibromopropylveronal



Merck.

Dial. Diallyl-barbituric acid

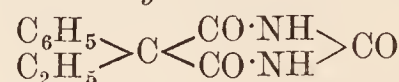


m.p. 170° (D. R. PP. 258058, 268158), Ciba.

For the reactions of Dial Ciba, see Isnard (J. Pharm. Chem. 1924, 29, 272; Analyst, 1924, 49, 287).

Proponal $(\text{C}_3\text{H}_7)_2\text{C}\begin{matrix} \text{CO}\cdot\text{NH} \\ >\text{CO} \\ \text{CO}\cdot\text{NH} \end{matrix}$ CO, dipropyl-barbituric acid, m.p. 145° , Merck and Bayer.

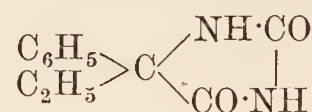
Luminal or *Phenylbarbital*



phenyl-ethyl-barbituric acid. Veronal in which an ethyl is replaced by a phenyl group. Stronger hypnotic (U.S. Pat., Bayer, 1025872, cancelled). The sodium salt is used hypodermically.

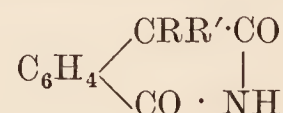
The hypnotic nucleus of these substances is evidently the urea radicle— $\text{HN}\cdot\text{CO}\cdot\text{NH}$ —when present in the cyclic form as a urcide; any change in the barbituric acid ring destroys the hypnotic action.

Nirvanol. $\gamma\cdot\gamma$ -Phcnylethyl-hydantoin



shows the same grouping— $\text{HN}\cdot\text{CO}\cdot\text{NH}$ —in a five-membered ring. It contains a CO group less than luminal and is of recent introduction. Synthesis, v. Read, J. Amer. Chem. Soc. 1922, 44, 1746.

Dialkylhomophthalimides of the type



in which RR' are two ethyl, two propyl, two allyl groups, or an ethyl and a propyl group, are hypnotics of very slight toxicity, free from

unfavourable secondary effects (Lumière and Perrin, Compt. rend. 1920, 171, 637).

SEDATIVES.

This group serves to reduce nervous hypersensibility as an aid in the general systematic treatment of diseases of the nervous system. According to the specific purpose for which these drugs are used, they may be divided into three classes, namely, bromine combinations, valeric acid esters, and derivatives of morphine.

Bromine combinations. When it is necessary to subject the system for a considerable period to the action of bromine and to avoid the undesirable secondary effects such as usually accompany the prolonged use of the alkali bromides, recourse may be had to the brominated fatty and albuminoid bodies. The decomposition of these derivatives usually takes place in the intestinal tract.

Bromipin. Bromine addition-product of sesame oil containing 10 and 33½ p.c. of bromine (D. R. P. 96495; U.S. Pat. 774224), Merck.

Bromlecithin. Brominated lecithin containing about 30 p.c. of bromine (D. R. P. 156110), Agfa.

Bromalbacid. Brominated albumin, 6 p.c. bromine, Gans.

Bromglidine. Brominated vegetable glidin, Klopfer.

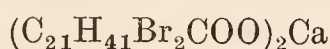
Bromocoll. A bromo-tannin-gelatin, 20 p.c. bromine, Agfa.

Bromolein. Brominated unsat. fatty acids of almond oil, 20 p.c. bromine.

Glycobrom. Glycerol ester of dibromocinnamic acid, Merck.

Lipobromol. Brominated poppyseed oil, 33 p.c. bromine.

Sabromin. Calcium dibromobehenate



29 p.c. bromine (U.S. Pat. 848230), Bayer.

Valeric acid derivatives. The replacement of a carboxyl hydrogen by alkyl radicles produces a distinctive narcotic effect, as instanced by ethyl acetate. Here it is evident that the acid radicle remains indifferent, while, on the other hand, the natural and synthetic esters of valeric acid exhibit the sedative effects of both groups. The well-known sedative action of valerian is due chiefly to the presence of the borneol ester of *iso*-valeric acid now sold as:

Bornyval. Bornyl *isovalerate*, b.p. 255°–260°, Riedel.

Bornyval, New. Bornyl *isovaleryl*glycollate



b.p. 181°/12 mm. Riedel.

Brophenin. Bromo-*isovaleryl*phenocoll. A brominated phenetidine derivative.

Brovalol. Bornyl α -bromo-*isovalerate*



American name for valisan, b.p. 163° (10 mm.) (U.S. Pat. 930504), Schering.

Eubornyl. α -Bornyl α -bromo-*isovalerate*, Luedy. =brovalol=valisan.

Substituting cinnamic acid for valeric, an excellent sedative has been obtained through combination with borneol, as:

Adamon. Borneol ester of dibromodihydrocinnamic acid



Bayer.

Gynoval. *Isoborneol* ester of *isovaleric* acid, b.p. 132°–138°/12 mm., no patent, Bayer.

Iodival. Mono-iodo-*isovaleryl*-urea, m.p. 180° (D. R. P. 197648), Knoll.

Quietol. Hydrobromide of dimethylamino-dimethyl-*isovaleryl* propyl ester, m.p. 105°–110°, when pure, 118°, Poulenc.

Valamine. *Isovaleric* ester of amylene hydrate



Merck.

Validol. Menthyl *isovalerate*; 30 p.c. free menthol, Zimmer.

Valisan. Bornyl α -bromo-*isovalerate*, Schering. =brovalol=eubornyl.

Valyl. Diethyl-valeramide



b.p. 210° (U.S. Pat. 697730), Hoechst.

Zeobromal. Dibromohydro-cinnamic ethylester

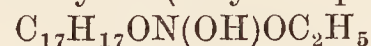


(D. R. P. 271434), Bayer, Merck.

The thymol ester of *isovaleryl*-glycollic acid (D. R. P. 260471), Riedel; also compounds of bromo-valeric acid and menthol, borneol and thymol (D. R. P. 263018).

Alpha-bromo-*isovaleric* amides of aliphatic primary amines (D. R. P. 261877), Liebrecht.

Synthetic morphine derivatives. The hydroxyl groups are intimately associated with the toxic action of morphine, which, through its narcotic characters, differs from all other opium alkaloids, its action being chiefly upon the nerve centres of the brain. Upon closing these OH groups by substituting one or both of the hydrogens by alkyl or acyl radicles, the narcotic characters disappear, while, on the other hand, a spinal excitant (tetanic) action is developed, increasing with the number of alkyls introduced. Thus, codeine produces, like morphine (but in lesser degree), narcosis, followed by an elevated reflex, which, if the dose be sufficiently large, develops tetanic convulsions. Other morphine esters, as codethyline (ethyl-morphine)



and thebaine $\text{C}_{17}\text{H}_{15}(\text{OCH}_3)_2\text{NO}$, the latter of which is the most toxic alkaloid of opium, are characterised by their action on the spinal cord, the tetanic effects being identical with those produced by strychnine. This action increases with the number and molecular weight of the alkyl groups introduced; hence codethyline with its ethyl group is more intense in action than codeine, which contains but one methyl group. The same may be said of the acyl compounds, those containing two such radicles are distinctly tetanic in action. Ethyl-morphine stands between morphine and codeine, being used as a sedative, especially for its action on the conjunctivæ.

Among all possible derivatives, it is immaterial whether an acyl or alkyl radicle, aliphatic or aromatic, is introduced; there is practically no qualitative difference in action so long as the same hydrogen is replaced. The more

readily the acid or alkyl group splits off from the nucleus, the more closely the properties of the derivative resemble those of morphine. On the other hand, too great a stability produces relatively inert bodies, morphine hydroxy-acetic, propionic or butyric acids are pharmacologically almost inactive, whereas, on the other hand, the methyl and ethyl esters of these acid derivatives produce intense picrotoxin-like convulsions, the seat of action being the *crura cerebri*. The mono-acyl derivatives (esters) of morphine, in which the phenolic hydrogen is replaced by acetyl or benzoyl groups, resemble morphine, being intermediate between it and the di-acyl derivatives as heroin.

Codeine, dionine, and peronine are ethers, since the phenolic hydrogen is replaced by CH_3 , C_2H_5 , and $\text{C}_6\text{H}_5\text{CH}_2$ groups. Those derivatives in which both hydroxyl groups are esterified by acyl groups possess a greater narcotic action than codeine, and stronger tetanic effect than morphine. They relieve spasmodic coughing, but are less active than morphine.

Winternitz¹ has shown that codeine and dionine produce no effect upon respiration, whilst the introduction of acid radicles increases the respiratory influence of morphine.

In all instances, the narcotic action of morphine is very much diminished, while the tetanic and also the action on the motor nerves are increased. The morphine derivatives of the codeine type, while less active in relieving pain, exert a sedative effect on the unstriated muscles of the bronchi and reduce the disposition to cough; hence are of value in phthisis, bronchitis, asthma, &c.²

Synthetic morphine derivatives may be classified as:

A. Ethers and esters—

Codeine, morphine methylether.

Ethyl morphine, codethyline, morphine ethyl ether.

Dionine. Ethyl morphine, U.S. P. Hydrochloride of the above.



m.p. 123° – 125° (D. R. P. 108075; no U.S. Pat.), Merck.

Peronine. Morphine benzylether hydrochloride



Merck.

Heroin. Diacetylmorphine, U.S. P. Diacetylmorphine hydrochloride



(no U.S. Pat.), m.p. 230° – 231° , Bayer.

Morphine esters of halogen fatty acids and esters derived from them, D. R. PP. 254094, 256156, von Heyden, e.g. the di- α -bromoiso-valeric ester.

B. Quaternary salts—

Eucodin. Codeine methobromide



m.p. 261° (D. R. PP. 166362, 175796), Riedel.

Morphosan. Morphine methobromide.



(D. R. PP. 165898, 191088), Riedel.

C. Dihydro derivatives—

Dihydromorphine is obtained by catalytic reduction of morphine with colloidal palladium (D. R. P. 278107), La Roche.

Paramorphan. Dihydromorphine hydrochloride (Knoll).

Paracodeine is dihydrocodeine hydrochloride (Knoll).

Paralaudin is diacetyl-dihydromorphine (Knoll).

Eucodal is dihydro-oxycodone hydrochloride



m.p. 270° (D. R. P. 296916). Acts like morphine, but more rapidly.

D. Molecular compounds and mixtures—

Narcodeon. Double salts of narcotine and codeine with di- and polybasic acids (D. R. P. 254502), Boehringer.

Codeonal. Molecular compound of codeine and veronal (Knoll).

Pantopon. A mixture of the hydrochlorides of all opium alkaloids, containing 50 p.c. of anhydrous morphine hydrochloride (U.S. Pat. 1056219), La Roche.

This is the most successful of a series of preparations of a similar nature; others are *Omnopon*, *Isopon*, *Somnopon*, *Laudanon*, *Nealpon*.

The imports of opium by firms licensed under the Dangerous Drugs Acts was 125,833 lbs. in 1923. The amount of morphine and its salts manufactured in 1923 was 254,337 ozs., of which 166,397 ozs. were converted into heroin, codeine, or other derivatives of opium, leaving a net total of 87,940 ozs., of which 78,611 ozs. were exported. The amount of heroin manufactured in 1923 was 11,575 ozs., and the total export of heroin was 12,011 ozs. The output of codeine in 1923 was 162,036 ozs., of which 160,910 ozs. were exported. As codeine was not subject to the Dangerous Drugs Acts, its movements were not recorded after it left the manufacturers, and it was not therefore known whether any other amounts of codeine were exported during 1923 by persons other than the manufacturers (J. Soc. Chem. Ind. 1924, 43, 749).

ALKALOIDS.

Quinine derivatives. All salts of quinine possess essentially the same medicinal action. The variety of new combinations that have appeared have been the result of attempts to correct unpleasant local and secondary effects, such as bitter taste, tinnitus, or stomach disturbances, and also to prepare soluble combinations suitable for hypodermic use.

To overcome local effects insoluble, tasteless compounds have been prepared, which pass unchanged through the stomach into the intestine, where they are broken up more or less rapidly into their components, producing accordingly a therapeutic action of greater or lesser intensity.

Therapeutically active radicles, such as salicylic acid, beta-naphthol, diethylbarbituric acid, &c., produce their specific effects.

¹ Therap. Monatsh, 1899.

² Pharmacology of morphine and codeine derivatives, Stockman and Dott, Brit. Med. J. 1890, ii. 189; Proc. Royal Soc. Edin. 1890, 321; Merck's Jahresber. 1898, 5.

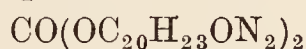
The local irritant action as well as slight solubility of the more common quinine salts which militate against their hypodermic use, have been overcome through very soluble double salts, such as quinine urea hydrochloride.

Insoluble quinine esters. These are esters in which the hydroxyl hydrogen of quinine has been replaced by various acid radicles. Being insoluble they are tasteless.

Aurochin. *p*-Aminobenzoyl-quinine

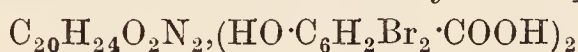


Aristochin. Diquinine carbonic ester, aristoquin



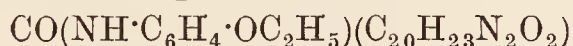
m.p. 189° (D. R. PP. 105666, 134307, 137308 ; U.S. Pat. 625075, expired), Bayer.

Bromochinol. Acid dibromosalicylate of quinine



m.p. 198°, Zimmer.

Chinaphenin. *p*-Ethoxyphenylcarbonic ester of quinine (from phenetidine)



(D. R. P. 109259), Bayer.

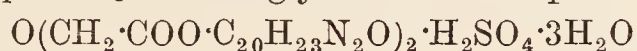
Chinaphthol. Quinine beta-naphthol-mono-sulphonate



m.p. 185°, Merck.

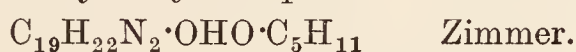
Chineonal. Quinine diethylbarbiturate contains 36 p.c. veronal, Merck.

Insipin. Quinine diglycollic ester sulphate



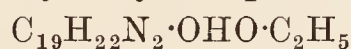
Merck.

Eucupin. Isoamyl-dihydrocupreine



Zimmer.

Optochin. Ethyl-dihydrocupreine



This differs from quinine in containing two more hydrogens and an ethoxy in place of a methoxy group. Optochin has a specific bactericidal effect on pneumococcus in vitro (U.S. Pat. 1062203), Zimmer.

Quineonal. See Chineonal.

Quinaphenin. See Chinaphenin.

Rheumatin. Salicylate of saloquinine, m.p. 183° (U.S. Pat. 698079, expired), Zimmer.

Saloquinine or *salochinin.* Quinine salicylic ester



m.p. 138° (U.S. Pat. 678401, expired), Bayer.

Soluble quinine salts. Adapted for hypodermic use.

Hydroquinine hydrochloride. Contains 2H more than quinine, very soluble, Zimmer.

Insipin hydrochloride. See Insipin.

Quinine and urea hydrochloride. See U.S. P.

Quinine dihydrochloride. See U.S. P.

Sinecain. Quinine hydrochloride and antipyrine.

Quinoline derivatives. The earlier attempts to determine the origin of the physiological action of quinine indicated that the quinoline nucleus was largely responsible. While this possesses an antiseptic and antipyretic action, the latter is much weaker and less reliable than that of quinine. In malaria quinoline is inert. The introduction

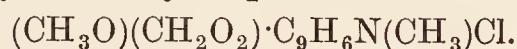
of a methyl group increases its antiseptic effect and diminishes antipyretic action, whilst the methoxyl, as in 6-methoxy tetrahydroquinoline (thalline), is markedly antipyretic. Owing to its injurious action upon the kidneys, the use of thalline was soon discontinued. A like course followed the introduction of the kairins, *N*-methyl and ethyl derivatives of 8-hydroxytetrahydroquinoline. The untoward effects of these remedies (toxic to red blood corpuscles) were not altered either through the introduction of other alkyls or acid radicles in the imino group. Quite different results were obtained by placing ethoxy and acylamino groups in the positions 1 : 4 (analgene), analogous to phenacetin. More successful derivatives of the class of hydroxyquinolines are found among the antiseptics, as loretin, diaptherin.

Quite different results have been attained through the introduction of a carboxylic group into the nucleus or its methylated derivative; such compounds possess not only analgesic action but also are of particular value in uric acid diathesis (see Atophan).

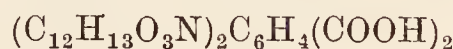
Miscellaneous alkaloids. Only those that have been the subject of recent research and patents are considered.

Narcotine ($\text{C}_{22}\text{H}_{23}\text{NO}_7$) on oxidation yields opianic acid and a base cotarnine $\text{C}_{12}\text{H}_{15}\text{O}_4\text{N}$. Hydrastine ($\text{C}_{21}\text{H}_{21}\text{NO}_6$), which differs from narcotine by absence of one OCH_3 group, on oxidation yields opianic acid and a base hydrastinine physiologically identical with and chemically similar to cotarnine.

Stypticin. Cotarnine hydrochloride, methoxymethylene-dioxy-isoquinoline methochloride.



Styptol. Cotarnine phthalate



(U.S. Pat. 742532), Knoll.

Hydrastinine hydrochloride $\text{C}_{11}\text{H}_{11}\text{O}_2\text{N} \cdot \text{HCl}$, m.p. 210°. A recent synthesis is based on condensing piperonal with amino-acetal, treating the piperonylideneamino-acetal with sulphuric acid which yields methylene-dioxy-isoquinoline, the methiodide of this on reduction yields hydrastinine hydriodide. (Preparation of bases as homopiperonylamine D. R. PP. 254860, 254861, 245523, 248046). For *N*-alkylacyl homopiperonylamine, (Anmeld, M. 470407 ; D. R. P. 257138). Hydrastinine from berberine (D. R. P. 259873 ; Anmeld, F. 33472). Recent Bayer patents are 267699, 234850, 270859, 267272, 257138.

The above products are valuable hæmostatics in uterine hæmorrhage.

Tetrahydrocolchicine. Prepared by catalytic reduction (with colloidal platinum) from colchicine. Less toxic than colchicine (D. R. P. 279999), L. Roche.

Urolysin. Iodo-*p*-phenetidine aceto-colchinine. Weitemeyer, Munich.

Atropine sulphuric acid. An internal ester of atropine $\text{C}_{17}\text{H}_{23}\text{O}_6\text{NS}$, m.p. 238°–239°. Less soluble and less toxic than atropine (Trendelenburg. Arch. exp. Path. Pharm. 1913, 73, 118). Used to suppress excessive salivation after narcosis. Decomposed by alkalis to apoatropine, La Roche.

ANTISEPTICS AND DISINFECTANTS.¹

Antiseptics are chemicals which have the power, in small quantities, to prevent infection or to arrest the multiplication of bacteria, and should be free from harmful action upon the human organism. Disinfectants destroy bacterial life and the noxious properties of putrefactive or fermentative products. Usually, small quantities of these chemicals are antiseptic, and large amounts disinfectant, in their effects.

The great variety of bacterial life, the kind, state, extent, composition, quantity, and condition of the associated matter, together with the difficulty of fixing, inhibiting and sterilising doses of disinfectants, makes the subject of standardisation of disinfectants perplexing and difficult. An ideal disinfectant must be able to destroy bacteria, be harmless to the human organism, penetrative, free from local irritation, toxic action and disagreeable odour. Very few, if any, of the disinfectants are adapted for universal use because of the great variety of conditions presented, hence each product is adapted for some special field of work.

Intestinal antiseptics are not attainable, because if the antiseptic were sufficiently powerful to destroy bacteria it must necessarily exhibit a toxic action on the human system. However, in certain lines, this class of antiseptics serve admirably in inhibiting the development of milder types of bacteria and neutralising the action of toxins in infections of the respiratory and urinary tracts. Combinations of bismuth and various antiseptics have become popular in treatment of intestinal disturbances due to fermentative changes or infection. To these must be added various compounds of beta-naphthol.

Inorganic antiseptics. More important and recent are fluorol (sodium fluoride), calcinol (calcium iodate), dymal (didymium salicylate), aluminium fluoride, iodine trichloride and tribromide, magnesium permanganate, vanadic acid, sodium perborate.

PEROXIDES.

Inorganic peroxides.² These peroxides represent hydrogen peroxide in which the hydrogen is replaced by metals, they readily decompose, under proper conditions, with liberation of hydrogen peroxide and oxygen. The advantages claimed over hydrogen peroxide are due to a more gradual liberation of oxygen, greater stability, convenience in form combined with a medicinal base. The medicinal peroxides are relatively insoluble in water, yielding weak alkaline solutions which evolve their oxygen slowly producing a continuous action. Internally, the alkaline earth peroxides are used as gastric and intestinal antiseptics in treatment of acid dyspepsia, abnormal fermentation, acidosis, also in dentifrices, while zinc peroxide, owing to the astringent properties of the base, is employed

in skin diseases. The commercial peroxides are usually mixtures of oxide and peroxide, hence vary in activity. Their relative oxidising powers vary in direct ratio to the alkalinity of the solutions produced in their decomposition (D. R. PP. 171372, 257535).

Hydrogen peroxide (*Perhydrol*) is a 30 p.c. solution (Merck).

Calcium peroxide, CaO_2 . A mixture of calcium carbonate, hydroxide, and not less than 60 p.c. of CaO_2 , equivalent to 13.3 p.c. of available oxygen.

Magnesium peroxide, MgO_2 (*Biogen*). A mixture of oxide, hydrated oxide, and not less than 15 p.c. of MgO_2 , equivalent to 4.3 p.c. of available oxygen.

Strontium peroxide, SrO_2 . This should contain at least 84 p.c. of SrO_2 , equivalent to 11.2 p.c. of available oxygen.

Zinc peroxide, ZnO_2 (*Dermogen* and *Ektogen*). Should contain at least 45 p.c. of ZnO_2 , equivalent to 7.4 p.c. of available oxygen.

Solids containing 35 p.c. of available H_2O_2 combined with urea are—

Perhydrit (Merck), *Ortizon* (Zahn & Co., Cologne) and *Hyperol* (Bayer, D. R. P. 259826).

Crystalline double compounds of $(\text{CH}_2)_6\text{N}_4$ and H_2O_2 containing 35 p.c. of active O, subject of D. R. P. 264111.

Organic peroxides. These represent oxides of organic radicles, which through hydrolysis yield peracids exerting marked oxidising and germicidal action through the slow evolution of nascent oxygen. These peroxides are used locally as antiseptics, and internally as intestinal antiseptics.

Acetozone. Acetyl-benzoyl peroxide diluted with an absorbent powder, m.p. 36.6° (U.S. Pat. 717016, expired), Parke, Davis.

Lucidol. Benzoyl peroxide.

Aluminium, organic salts. These combine the astringent properties of aluminium salts with the disinfectant action of the respective organic acids. They are relatively non-toxic, owing to lack of absorption, and astringent, because of their property of precipitating protein.

The following salts have no special advantage over ordinary aluminium acetate:—

Aluminium aceto-tartrate ‘ <i>Alsol</i> .’	Aethenstaedt.
„ salicylate ‘ <i>Salumin</i> .’	Riedel.
„ zinc acetate ‘ <i>Zinol</i> .’	Lewinsohn.
„ boro-tartrate ‘ <i>Boral</i> .’	
„ chlorate, ‘ <i>Mallebrein</i> .’	
„ formate ‘ <i>Alformin</i> .’	Elb.
„ formaldehyde-sulphite ‘ <i>Moronal</i> .’	
„ gallate, basic, ‘ <i>Gallal</i> .’	Riedel.
„ β -naphthol disulphonate ‘ <i>Alumnol</i> .’	(D. R. P. 74209) Hoechst.
„ <i>p</i> -phenol sulphonate ‘ <i>Sozal</i> .’	
„ potassium salicylate ‘ <i>Alkasal</i> .’	Aethenstaedt.
„ sodium acetate ‘ <i>Acetonal</i> .’	Aethenstaedt.
„ di-iodo- <i>p</i> -phenolsulphonate	Trommsdorf.

Bismuth organic salts. These, because of their insolubility, serve mechanically as protectives for inflamed or irritated surfaces as in wounds, gastric or intestinal disturbances. From fresh wounds bismuth may, however, be

¹ Standardising of Disinfectants, J. Royal Institute of Public Health, London, 1908; Experimentelle Pharmakologie, H. Meyer and R. Gottlieb, Berlin and Vienna, 4th ed. 1920, p. 564 *et seq.*; Jour. Hygiene, London, vol. viii. No. 5, Chick and Martin; Jour. Amer. Medical Assoc. vol. lv. p. 1635, Post and Nicoll.

² Catalyzers from animal and plant kingdom (D.R.P. 258880).

absorbed, and cause poisoning, like that due to mercury. Bismuth salts also serve, when combined with phenols or their derivatives (betanaphthol, tribromophenol, &c.), as excellent intestinal disinfectants, owing to their fine state of subdivision, which favours an even deposition throughout the tract. Soluble bismuth salts are of doubtful value. The U.S. patents on the more important products have expired. Only those sold under registered names are given.

There is hardly more *raison d'être* for these than in the case of the above-mentioned aluminium salts. The best known are dermatol (the oldest), xeroform and airol.

Bismuth albuminate 'Bismutose'	Kalle.
„ bilacto-monotannate 'Lactanin.'	
„ bitannate 'Tannismut'	Heyden.
„ borophenate 'Marcasol.'	
„ bromogallate.	
„ chrysophanate 'Dermol.'	
„ cinnamate 'Hetoform'	Kalle.
„ colloidal 'Bismon'	Kalle.
„ dithiosalicylate 'Thioform'	Speyer.
„ gallate 'Dermatol.'	
„ gallocarbonate	Bayer.
„ iodo-resorcin-sulphonate 'Anusol'	Schering.
„ „ gallate 'Airol'	La Roche.
„ „ salicylate 'Iodylin.'	
„ „ tannate 'Ibit'	Agfa
„ methylene digallate 'Bismal'	Merck.
„ β-naphtholate 'Orphol'	Heyden.
„ salt of tetra-iodophenolphthalein 'Eudoxin'	Rhenania.
„ para-nucleate 'Parabismut.'	
„ pyrogallate 'Helcosol'	Merck.
„ quinoline-sulphocyanate 'Crurin'	Kalle.
„ tetrabromocatechol 'Noviform'	Heyden.
„ tribromophenate 'Xeroform'	Heyden.

A novel, and probably important, application of bismuth is as *sodium bismuth tartrate*, which analogue of tartar emetic is injected, suspended in oil, in syphilis (Sazerac and Levaditi, *Compt. rend.* 1921, 172, 1391; 173, 338). *Bischlorol* is microcrystalline bismuth oxychloride in camphor water, recommended for the same purpose.

Mercurial antiseptics and mercurials. The value of mercury in treatment of syphilis and also as an antiseptic has brought out a great variety of combinations, some of which, because of their ready solubility, freedom from irritation, and slow elimination from the system, are especially adapted for subcutaneous and intramuscular injection. Others represent antiseptics equal in value to corrosive sublimate yet free from its objectionable action on instruments. With a few exceptions, only such as are marketed under registered names are enumerated. Others are given in Merck's List.

Advance in mercurial therapy during recent years has been chiefly either in the perfection of hypodermic usage or the introduction of organic compounds which seem to be less irritating to the gastro-intestinal tract than the inorganic salts. The less soluble salts require less frequent injection owing to slow absorption. Monophenol mercury, which is quite unstable in the body, is a valuable mercurial, whilst the diphenyl compound is very poisonous because of

its cumulative action. Dimethyl and diethyl mercury are similar.

The intramuscular injection of mercury has found much favour, employing colloidal calomel, colloidal mercury, mercury derivatives of acid amides and amino-acids, especially of succinimide (Hydrargol), also secondary mercury salicylate which yields soluble double salts with alkali chlorides. Excellent results have been obtained with mercury protein compounds. Also Hydrargyrol (*p*-phenol sulphonate) does not precipitate proteins. Its double salt with ammonium tartrate (Asterol) is more stable, does not cauterise or precipitate protein and penetrates readily into tissue.

Organic compounds of mercury may be divided into four classes: (1) mercury readily removed by hydrogen sulphide and alkaline hydroxides; (2) removed by hydrogen sulphide, but not by alkali hydroxide (pseudo-complexes); (3) mercury directly united to one carbon atom (half-complexes); (4) mercury between two carbon atoms (full complexes). The last are therapeutically the most interesting (Schoeller and Schrauth, *Mediz. Klinik.* 1912, No. 29). Cf. other papers by these authors: *Zeitsch. f. Hygiene u. Infektionskr.* 1910, 66, 417; 1911, 70, 24; 1916, 82, 279; *Ber.* 1919, 52, 1777; 1920, 53, 634; also their patents, e.g. D. R. P. 339494 of 1921. Further, Blumenthal and Oppenheim, *Biochem. Zeitsch.* 1912, 39, 58; 1913, 57, 260; 1914, 65, 460 (physiological action). Finally, *Organic Compounds of Mercury*, by F. C. Whitmore, 1921.

Anogon. Mercury-salt of diiodo-*p*-phenolsulphonic acid (30 p.c. iodine and 50 p.c. mercury), Trommsdorff.

Antiperiostin. Mercury iodocantharidate (D. R. P. 193219), A. Klein, Berlin.

Apallagin. Mercury nosophen (tetra-iodo-phenolphthalein), Hoechst.

Asiphyl. Mercury atoxyl.

Argulan. Dimethyl-phenyl-pyrazolone mercury sulfamate (D. R. PP. 257315, 261081, 261082).

Asterol. Mercury *p*-phenol sulphonate with ammonium tartrate (D. R. P. 104904), La Roche.

Enesol. Mercury salicylo-arsenate, Clin & Co., Paris.

Hermophenyl. Mercury sodium disulphonate, Merck.

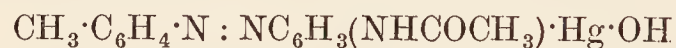
Hydrargol. Mercury succinimide, Gehe Co.

Hydrargotin. Mercury tannate, Hell Co.

Hydrargyroseptol. Quinoline mercury-sodium chloride, Fritzsche.

Lévurargyre. Mercury nucleoproteid, Adrian, Paris.

Mat. A lipotropic mercury compound, 4-*p*-tolueneazoacetanilide-3-mercurihydroxide



It is preferentially taken up by the central nervous system (Hüsgen, *Biochem. Zeitsch.* 1920, 112, 1).

Mercuriol. Mercury nucleate (U.S. Pat. 637355), Parke, Davis.

Mercochinol. Mercury hydroxyquinoline sulphonate, Fritzsche.

Mergal. Mercury cholate with albumin tannate (U.S. Pat. 811193), Riedel.

Mercury guaiacol sulfonate.

Mercury alpha-aminobutyrate (D. R. P. 306198).

Merlusan. A mercuric albumin compound
Bayer, Budapest.

Meriodin. Identical with anogon.

Phenegol. Mercury potassium *p*-nitrophenol
sulphonate.

Sublamine. Mercuric sulphate ethylenediamine
(U.S. Pat. 726126), Schering.

Sodium diamino-diphenyl-mercuridicarboxylate
38 p.c. Hg. (Blumenthal, Biochem. Zeitsch.
1911, 32, 59).

Thymegol. Mercuric potassium thymol sul-
phonate.

Toxynon. Sodium acetamino-mercuric ben-
zoate, Charlottenburg.

Dioxy-diamino-mercuro-benzene, analogous to
salvarsan



The following patents have been taken out
on new combinations :—

Mercury salt of tyrosine, La Roche (D. R. PP.
267411, 279957). Para-nuclate of mercury
and tannin, Kalle, 272688.

Mercury amino compounds, Riedel, 279199.
Mercurous compounds of basic purines,
Anmeld R., 39576, Kl. 12, p. 120.

Mercury substitution compounds in aryl oxyfatty
acids (D. R. P. 261229), and in aromatic oxy-
acids (D. R. P. 264388). Nucleus substitution
of amino-benzoic derivatives (D. R. P. 261460).
Soluble and alkali-resistant mercuric amino
sulphonic acids (D. R. PP. 261081, 261082,
266578).

Copper compounds.

Copper salt of d-alanine.

Cuperatin. Copper albuminate.

Cupriaseptol. Copper *m*-phenolsulphonate, Ga-
walowski, Berlin.

Cuprol. Copper nuclate, Parke Davis.

Lecutyl. Copper lecithin, Bayer.

These have mostly been tried in cancer and
in protozoal diseases, without success.

MISCELLANEOUS SALTS AND COLLOIDAL METALS.

Colloidal metal suspensions are employed
chiefly hypodermically for intramuscular injec-
tions.

Electricidal. Electro-colloidal iridium.

Nizin. Zinc sulphanilate, Burroughs.

Vanadiol. Vanadium hypochlorite for anæmia.

Oxynitro zanibeletti. Colloidal hydrated man-
ganese peroxide. Used in cholera.

Leptynol. Colloidal palladious hydroxide sus-
pended in oil. Used for obesity.

The following colloidal suspensions have been
proposed in treatment of cancer: Electroselen;
electro-iridol; Santon (Rd); electro-mercuro-
l; electromartiol (Fe); cuprase (oxyhydrated
copper); thiarsol (As_2S_3).

Mercurous compounds.

Calomelol. Colloidal form of calomel containing
protein (U.S. Pat. 740855), Heyden.

Mercoïd. Suspension of calomel and mercury
salicyl-sulphonate.

Metallic Mercury.

Electromercuro-l. A colloidal suspension of
mercury (prepared by electrical dispersion)
equivalent to 0.1 p.c. of Hg., Fougere, N.Y.

Hyrgol. Colloidal mercury, Heyden.

Mercuriol. Mercury amalgam with aluminium.

Organic silver antiseptics. Silver salts are

employed to produce caustic, astringent, germi-
cidal and antiseptic effects. Where a caustic
action is desired, silver nitrate is given the
preference, but in the treatment of infected and
inflammatory conditions of mucous surfaces,
this salt possesses an irritating and caustic
action which greatly restricts its usefulness.
Apart from this, it has only a limited penetrating
power, due to the fact that it is precipitated by
protein and sodium chloride, ordinary con-
stituents of tissues and their secretions. This
is a serious disadvantage, since many of the
conditions in which it is employed are due to
micro-organisms, which are found not only in
the superficial, but also in the deeper portions
of the mucous surfaces, and hence cannot be
reached by solutions of this chemical, owing to
the formation of an insoluble silver albuminate
in the upper layers. The recognition of these
drawbacks has led to the many new organic
compounds of silver now on the market. The
older organic salts have been practically super-
seded by the protein compounds. They
reproduce the antiseptic action of silver nitrate
to a certain degree according to their silver
content; are unaffected by either proteins or
chlorides, being used for the prophylaxis and
treatment of sensitive mucous surfaces as in
gonorrhœa, conjunctivitis, and other infections
of the urethra, eye, ear, nose, and throat. The
protein silver compounds should never be boiled,
nor mixed with drug extracts.

Silver protein compounds.

Albargin. Gelatose silver (15 p.c. silver) (D. R. P.
146792; U.S. Pat. 681482), Hoechst.

Argonin. Cascin silver (4.3 p.c. silver) (U.S.
Pat. 575277), Hoechst.

Argyrol. A compound of derived protein and
silver oxide (20–25 p.c. silver), Barnes.

Hegonon. Ammonio-silver nitrate albumose (7
p.c. Ag) (U.S. Pat. 567412), Schering.

Nargentol. Silver protein, Larimer, London.

Nargol. Silver nucleate (10 p.c. silver), Parke
Davis.

Novargan. Silver proteinate (10 p.c. silver)
(U.S. Pat. 19989), Heyden.

Omorol. Protein silver (10 p.c. silver),
Heyden.

Protargol. Protein silver (8.3 p.c. silver) (U.S.
Pat. 615970, expired), Bayer.

Solargyl. Compound of Ag_2O and proteoses,
30 p.c. Ag., Luedy-Bergdorf, Sw.

Sophol. Methylene nucleic acid silver com-
pounds (20 p.c. silver) (D. R. P. 825545),
Bayer.

Silver salts. *Argochrom* (Methylene blue silver);
Citrate (*Itrol*, Heyden); eosolate (acetyl-
guaiacol-tri-sulphonate); fluoride (*Tachiol*);
lactate (*Actol*, Heyden); picronitrate (*Picra-
tol*, Wyeth); *sulphophenate* (Silberol). Com-
plex silver salts of α -amino acids (Napp, Eng.
Pat. 148074, 1921).

Argentamine. Ethylenc-diamine silver nitrate
(10 p.c. silver nitrate) (D. R. P. 74634),
Schering.

Argentol. Silver quinaseptolate (31.7 p.c.
silver), Fritzsche.

Ichthargan. Silver sulphoichthyolate (30 p.c.
silver), Merck.

Colloidal silver preparations.

Colloidal silver is not precipitated by
proteins, chlorides, or other precipitants of

silver salts, hence its solutions may be used with various organic solutions and injected into the tissues without precipitation or causing any irritation. They possess the antiseptic properties of the silver compounds.

Cargentos. Colloidal silver oxide containing an equivalent of 50 p.c. of metallic silver (U.S. Pat. 1043646), Mulford.

Collargol. Colloidal silver containing approximately 78 p.c. of Ag, Schering and Glatz.

Choleval. Colloidal silver containing sodium cholate, Merck.

Dispargen. Colloidal silver, Reisholz, Duesseldorf.

Electrargol. Colloidal silver suspension containing 0.04 p.c. Ag, Fougere, New York.

Electrocollargol. Colloidal silver in suspension, Heyden.

Fulmargin. Electric colloidal silver, Rosenberg, Charlottenberg.

Lysargin. Colloidal silver, Kalle.

Skiargan. Conc. colloidal solution, Heyden.

Solargentum. Colloidal-gelatin silver (19 to 23 p.c. Ag), Squibb.

Syrgol. Colloidal Ag_2O suspension, Siegfried.

Organic gold compounds.

Gold cyanide was found by Koch to inhibit the growth of tubercle bacilli at very great dilution (1 : 2,000,000), but only *in vitro*. Any therapeutic effect is probably due to colloidal gold formed in the tissues. Complex gold salts of bases (ethylene-diamine, hexamethylene-tetramine, salvarsan) have been tried.

Aurocantan. Monocantharidylethylene-diamine auricyanide.

Krysolgan. Sodium 4-amino-2-auriphenol-1-carboxylate inhibits tubercle bacilli *in vitro* at 1 : 1,000,000.

Inorganic salts of nucleic acids. The nucleins are complex combinations of protein groups and nucleic acid. Commercial nucleins vary in composition according to the process employed in their extraction, prolonged or stronger treatment causes nuclein, through the elimination of the protein molecule, to assume a composition nearer that of nucleic acid. The nucleic acids are definite chemical compounds of very complex structure. Nucleic acid, a substance common to the blood corpuscles, organs, and vital tissues of the animal organism, has suggested itself as a means for the more ready and effectual administration of metals. The hypothesis that inorganic salts of the heavy metals pass into the blood only in so far as they combine with the nucleic acid, would seem to offer sufficient ground for the artificial preparation of derivatives which would be more readily absorbed and utilised in the human organism. Apart from this, certain of these combinations are especially adapted for external use as antiseptics because of their penetration, freedom from irritation and decomposition by contact with proteins. These combinations comport themselves quite differently from the other more common organic salts, in that the usual inorganic reagents fail to produce any of the characteristic qualitative reactions. For example, copper nucleate fails to turn blue upon the addition of ammonia water, nor does it react with hydrogen sulphide. The addition of chlorides fails to precipitate silver from these organic combinations.

Nucleic acid may be obtained from the wheat embryo, the pancreas, thymus glands, and yeast. In outline, the process of isolation consists in digesting the ground organs at boiling heat with a 2 p.c. NaOH solution containing 10 p.c. of sodium acetate. After one hour, filter hot, concentrate, neutralise with acetic acid, which does not precipitate the ordinary nucleic acids, filter again. From this filtrate the crude salts are obtained by precipitation with alcohol and washing with the same. The salts are finally dissolved in hot water and decomposed with dilute HCl which precipitates the free nucleic acids. In such combinations as the nucleate or other protein derivatives of the metals, the latter are retained in the protein molecule in a masked state beyond the reach of the usual inorganic reagents. In the case of the iron preparations we have a ready means of distinguishing this masked metal from that present in the form of the ordinary organic salts, as the peptonate, lactate, &c., in the well-known Macallum's test. This consists in adding a few drops of a 1 p.c. solution of hæmatoxylin to the solution of the preparation, whereby a blue to blue-black coloration ensues if it belongs to the latter class.

The nucleic acids are insoluble in water, alcohol, ether, or other organic solvents. Their alkali salts are soluble in water, especially so in presence of sodium acetate. Salts of the heavy metals are insoluble. The pure acids do not give the biuret nor Millon's reaction, the nucleins, however, respond owing to the presence of protein residues. It is claimed that the nucleins increase the number of white corpuscles, hence are of value in treating infections. **Nuclein.** A modified nucleo-protein obtained by peptic digestion or treatment with dilute acids.

Nucleic acid. An organic acid obtained from nuclein by action of alkalis or by tryptic digestion.

Cuprol, *Mercuriol*, *Nargol*, are respectively the copper mercury and silver salts of nucleic acid, Parke Davis.

Ferratogen is the iron salt, Ciba.

Organic iodine derivatives. *External iodoform type.* The organic iodine combinations are employed in treatment of wounds, granulated surfaces, abscesses, &c., their action being due to stimulation of phagocytosis and diminished secretion of the surface, which becomes thereby a less favourable culture medium for germs. Compounds like iodoformin and iodoformal, which break up into their components through contact with water, present no advantages over simple mixtures. Apparently, the replacement of H by iodine in aromatic antiseptics would increase their bactericidal power, however, when this replacement takes place in the nucleus, the iodine is too firmly united to be liberated by tissue secretions.

For this reason, the iodo-phenols do not offer any advantages over the phenols, further, Iosophan, tri-iodo-*m*-cresol (containing an unsubstituted hydroxy group) in which 3 hydrogen atoms of the nucleus are replaced by iodine, possesses the antiseptic action of phenols in a marked degree, yet does not exhibit any iodine action. On the other hand, the iodoxyl group (OI) possesses marked antiseptic and antisiphilitic properties. The best known examples of

iodoxyl substitution are aristol, euophen, and isoform, all of which liberate iodine.

The bactericidal effect of this group depends upon the action of the alkaline wound secretions in splitting up the compounds into their component parts. Iodoform is antiseptic only under conditions in which iodine is slowly eliminated. The newer combinations have aimed at overcoming the objectionable odour and occasional tendency to iodine poisoning peculiar to iodoform, also to combine a lower percentage of iodine with an antiseptic nucleus, securing thereby a milder iodine effect in conjunction with that of the nucleus.

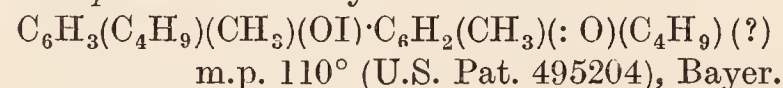
Aristol. Dithymoldiiodide



Chrysoform. Dibromo-diiodo-hexamethylene-tetramine Merck.

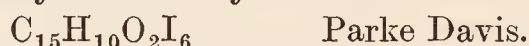
Diiodoform. Tetra-iodo-ethylene, C_2I_4 , Schering.

Euophen. Diisobutyl-cresol iodide



m.p. 110° (U.S. Pat. 495204), Bayer.

Formidin. Methylene-disalicylic iodide



Griserin. Isomeride of loretin (D. R. P. 187943) Griserin Werke, Berlin.

Iodanisol. o-Iodo-anisole $C_6H_4I \cdot OCH_3$, m.p. 47°, Merck.

Iodocrol. Carvacrol iodide $C_{10}H_{13}OI$, Merck.

Iodoformal. Iodoformin ethyl iodide, m.p. 128° (D. R. PP. 87812, 89243), Marquart.

Iodoformin. Hexamethylenetetramine iodoform $CHI_3(CH_2)_6N_4$, m.p. 178°, Marquart.

Iodoformogen. Iodoform albumin (D. R. P. 95580), Knoll.

Iodogallicin. Bismuth hydroxyiodidemethyl gallol $C_6H_2(OH)_2(COOCH_3)(OBi \cdot OH)$ Sandoz.

Iodol. Tetraiodopyrrol C_4I_4NH (D. R. P. 35120), Kalle.

Iodolen. Iodised albumin. Kalle.

Iodolin. Quinoline chloromethyl-iodo-chloride.

Iodophenin. Iodophenacetin, m.p. 130° (D. P. R. 58404), Riedel.

Iodothymoloform. Iodised thymoloform, m.p. 150°, Henning.

Iodozol. Sozoiodolic acid (diiodo-*p*-phenolsulphonic acid) $C_6H_2I_2(OH)SO_3H + 3H_2O$ Trommsdorf.

Iothion. 1, 3-di-iodo-propane-2-ol $CH_2I \cdot CH(OH)CH_2I$ Bayer.

Isoform. *p*-Iodoxy-anisole $C_6H_4(OCH_3)IO_2$ (D. R. P. 161725), Hoechst.

Loretin. 3-Iodo-4-hydroxyquinoline-1-sulphonic acid (D. R. P. 72294), Schuchardt.

Losophan. Tri-iodo-metacresol $CH_3 \cdot C_6HI_3 \cdot OH$ m.p. 121°, Bayer.

Nosophen. Tetra-iodo-phenolphthalein (D. R. PP. 86069, 143596), Rhenania.

Novoiodin. Hexamethylene-tetramine-di-iodide.

Sanoform. Di-iodo-salicylic methyl ester $C_6H_2(COOCH_3)(OH)I_2$ m.p. 110·5°, Hoechst.

Septovince. Tri-chlor-acetyl-di-phenol-di-iodide.

Traumatol. Mono-iodo-cresol, Chevrier and Kraus, Paris.

Vioform. Iodo-chloro-hydroxyquinoline $C_9NH_6(OH)ICl$ (D. R. P. 117767), Ciba.

For internal use.—These preparations are of special interest in iodide therapy; being chiefly compounds of iodine with proteins and

fats, they are far less irritating to the digestive tract, and under ordinary conditions, less liable to produce symptoms of iodism.

Alival. 1 : 2-Dihydroxy-3-iodopropane, used with salvarsan, Hoechst.

β-Eigon, an iodised peptone.

Ferro-sajodin (basic ferric iodobehenate) (5 p.c. to 24 p.c. iodine), Bayer.

Iodalbacid. Iodised albumin (10 p.c. iodine), Gans.

Iodalbin. Iodised albumin (21·5 p.c. iodine), Parke Davis.

Iodeigon. An α-iodised albumin (20 p.c. iodine), sodium salt (15 p.c. iodine), Helfenberg.

Iodglidin. Iodised gluten (10 p.c. iodine), Klopfer.

Iodin. Iodised arachis oil.

Iodipin. Iodised sesamé oil (10 and 25 p.c. iodine) (D. R. P. 96495), Merck.

Iodival. Iodo-monoiso-valeryl-urea $(CH_3)_2CH \cdot CHI \cdot CO \cdot NH \cdot CO \cdot NH_2$ m.p. 180° (D. R. P. 197648), Knoll.

Iodo-casein (18 p.c. iodine), Mulford.

Iodoglobin. Di-iodotyrosine $HO \cdot C_6H_2I_2 \cdot CH_2 \cdot CH(NH_2)COOH$ La Zyme, St. Ludwigswitz.

Iodolecithin, 7 to 8 p.c. iodine (D. R. P. 155629), Riedel.

Iodomenim. Iodised casein containing bismuth (10 p.c. iodine) (D. R. P. 177109), Wuelfing.

Iodtriferrin. Iodised paranucleate of iron (15 p.c. Fe, and 8·5 p.c. I) (D. R. P. 258297), Knoll.

Iodyloform. Iodised gelatin (10 p.c. iodine), Kohlmeyer.

Lipoiodine. Ethyl ester of di-iodo-brassicidic acid



(41 p.c. iodine), Ciba.

Sajodin. Mono-iodo-behenate of calcium



(5 p.c. iodine) (U.S. Pat. 839509). Iron sajodin, see Ferro-sajodin, Bayer.

Siomine. Hexamethylenamine tetra-iodide $(CH_2)_6N_4I_2$

(78·5 p.c. iodine) (U.S. Pat. 1226394), Howard Holt, Cedar Rapids, Iowa.

Taririnic acid diiodide $C_{22}H_{32}O_2I_2$. Analogous to Lipoiodin (D. R. P. 261211; Ber. 24, 4116), La Roche.

Tiodin. Addition product of allylthiourea (thiosinamine) and ethyliodide



Formaldehyde derivatives. Formaldehyde is still sold under registered names such as Formal, Formysol, Holzin, Camolin, Methylal, Steresol, Vesoform. It has virtually supplanted all other embalming fluids. Locally, formaldehyde is an irritant and coagulent, hence many attempts have been made to prepare stable combinations to which it readily lends itself. The purpose being that such compounds, when brought into contact with wound secretions, would break up with a very gradual liberation of formaldehyde. The difficulty encountered has been to secure such a degree of stability that formaldehyde will be liberated in a concentration sufficient to

maintain antiseptic action without becoming irritant. Results in this direction have not been very successful except in the instances of such products as Formicin, Fortoin, and Euguform. Hexamethylenetetramine cannot be included among these, since it breaks up only in acid media, hence it has found general use as a urinary disinfectant (*vide*). Some of these formaldehyde condensation and addition products owe their value more to the other constituent than to the formaldehyde, as, for instance, Empyroform, Phenyform, Thymolform, &c.

Amyloform. Formaldehyde-starch (D. R. P. 92259), Gans.

Chinoform. Cinchotannic-acid-formaldehyde, also quinine formate.

Cresoform. Condensation product of creosote and formaldehyde.

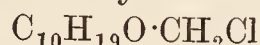
Empyroform. Formaldehyde tar condensation product, Schering (U.S. Pat. 761260).

Euformol. Formaldehyde-dextrin.

Euguform. Acetylated methyleneguaiacol, Guestrow.

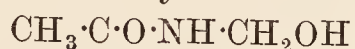
Formaldehyde casein, Merck.

Forman. Chloro-methyl menthyl ether



b.p. 160° (16 mm.) (D. R. P. 119008), Lingner.

Formicin. Formaldehyde acetamide compound,



(D. R. P. 164610), Kalle.

Fortoin. Methylene-dicotoin (D. R. P. 104362).

$\text{CH}_2(\text{C}_{14}\text{H}_{11}\text{O}_4)_2$ m.p. 211°–213°, Zimmer.

Galalith. Formaldehyde casein, Galalith Co., Frankfurt.

Hetroform. Condensation product of formaldehyde and benzoic acid.

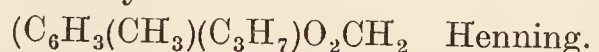
Methylol carbazole. Action of formaldehyde on carbazole (D. R. P. 256757), M. Lange, Frankfurt.

Phenyform. Condensation product of formaldehyde and phenol $[\text{C}_6\text{H}_4(\text{OH})\text{CH}_2\text{OH}]_x\text{CH}_2\text{O}$
Phenyform Co., Berlin.

Tannoform. Methylene-ditannin $\text{CH}_2(\text{C}_{14}\text{H}_9\text{O}_9)_2$
(D. R. P. 88841), Merck.

Theoform. Condensation product of theobromine and formaldehyde.

Thymolform. Condensation product of formaldehyde and thymol



Compounds obtained through the action of metallic hydroxides on formaldehyde are the subject of D. R. P. 277437. Through action of paraformaldehyde on sugar under pressure (Bauer & Co., D. R. P. 280091).

Sulphurated products. Salts of sulphonated tars obtained by the destructive distillation of fossilised fish or certain bituminous shales are used as antiseptics. They contain a high percentage of sulphur present as sulphides, sulphones, and sulphonates. The first of this class to be introduced was:

Ichthyol, i.e. the ammonium salt of so-called ichthyol-sulphonic acid obtained by sulphonating the fossilised fish-tar (D. R. P. 35216). Ichthyol should contain at least 5.5 p.c. of 'organic' (sulphid) sulphur. Other combinations are *ichthalbin* (ichthyol albumin) (Eng. Pat. 11344), *ichthargan* (ichthyol-silver) (Eng. Pat. 11344), *ichthermol* (ichthyol mercury), *ichthoform* (ichthyol formaldehyde) (D. R. P.

107233), *ichthyolidin* (piperazine ichthyolate), calcium, sodium, and ferric ichthyolate, Cordes and Merck.

Products of similar nature are *isarol*, *petrosulfol*, *sulfogenol*, *ichthosulfol*, *ichthynat*.

Ittiolo. Ammonium sulphoichthyolate prepared from the bituminous shales of Giffoni Vallepiana, Italy, G. W. Guidi, N.Y.

Nafalan, similar to naftalan, Nafalan Co., Magdeburg.

Naftalan. Distillations-residue, free from resin and asphalt, obtained from Caucasian petroleum mixed with sodium stearate, Naftalan Co., Dresden.

Sulfidol. Colloidal sulphur (D. R. P. 164664), Heyden.

Thiogenol. A solution of the sodium salts of synthetic sulpho-oleic acids, containing 2.85 p.c. of sulphur, La Roche.

Thiol. Sulphurated and sulphonated paraffin oil (D. R. P. 38416), Riedel.

Tumenol. A sulfonated oil obtained by the distillation of bituminous shale (D. R. P. 56401), Hoechst.

SELENIUM COMPOUNDS.

A supposed favourable effect of a dye containing selenium on mouse cancer, recorded by A. von Wassermann, has led to the preparation of a large number of organic selenium compounds, although none appear to be of any real value. The true selenium analogue of methylene blue closely resembles its sulphur prototype, and like it is a vital stain (Karrer, Ber. 1916, 49, 597). Selenium compounds are the subject of the following patents, *inter alia*: D. R. PP. 255982, 261969, 290540, 299510, Hoechst; 256667, 264139, 264940, 264941, Bayer.

HYPOCHLORITES AND CHLORINE ANTISEPTICS.

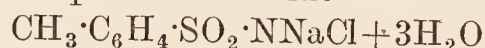
The alkali hypochlorites have been used many years as disinfectants. Carrel and Dakin extended their application to the treatment of infected wounds, pointing out, however, the fact that these solutions should not only be neutral (as alkalinity causes destruction of tissue and skin irritation), but also should not contain less than 0.4 p.c. nor more than 0.5 p.c. of sodium hypochlorite, the weaker solution being devoid of germicidal power, while the latter irritates.

Antiformine. A strongly alkaline solution of NaOCl equivalent to 5.6 p.c. of Cl. Used as local disinfectant and antiseptic (U.S. Pat. 691671), Amer. Antiformin Co.

Hychlorite. A solution of sodium hypochlorite equivalent to 3.8 p.c. available Cl, Gen. Lab., Madison, Wisc.

Owing to the uncertainties attending the preparation and keeping of such inorganic solutions, organic compounds containing the chloramino group (discovered by Chattaway¹) which are neutral, non-irritating and stable, have become popular. These chloramines are prepared by the action of hypochlorite solutions on amides.

Chloramine-T (Chlorazene).² Sodium para-toluene sulpho-chloroamide



¹ Trans. Chem. Soc. 1905, 87, 145.

² Brit. Med. J. 1915, Aug. 25; 1916, Jan. 29.

This is used in 0.1 to 4 p.c. aqueous solution. Method of preparation (Inglis, J. Soc. Chem. Ind. 1918, 37, 288 T).

Chloramine B. Sodium benzene sulfo-chloro-amide $C_6H_5 \cdot SO_2 \cdot NNaCl + 2H_2O$. Used like Chloramine-T, Calco Chem. Co., Bound Brook, N.J.

*Chlorcosane.*¹ A liquid chlorinated paraffin wax containing Cl in non-active combination. This is used as a solvent for dichloramine-T in 8 p.c. solutions. The Cl content is from 27 to 35 p.c. Chlorinated eucalyptol is employed for like purposes.

*Dichloramine-T.*² Para-toluene-sulphon-dichloramide $CH_3 \cdot C_6H_4 \cdot SO_2NCl_2$. This is used in 2 to 10 p.c. solutions in chlorcosane or chlorinated eucalyptol.

*Halazone.*³ Para-sulphon-dichloramido-benzoic acid $HOOC \cdot C_6H_4 \cdot SO_2NCl_2 \cdot 1:4$. For sterilising water 0.004 to 0.008 gm. halazone in tablets containing sodium carbonate (or borate) and sodium chloride is added to 1 litre.

ANTISEPTICS CONTAINING PHENOL NUCLEI.

During the last few years very few new derivatives of this class have appeared, although much work has been accomplished in tracing the groups to which their destructive action on pathogenic bacteria is due. The caustic action of phenol on the skin and mucous surfaces resides, without doubt, in the hydroxyl group which is also common to its homologues. The local antiseptic properties decrease with an increase in the number of hydroxyl groups as is the case with resorcinol and pyrogallol. Their toxicity increases with the number of hydroxyls. The relative positions occupied by these groups determines likewise relative toxicity, thus the *o*-dihydroxybenzene (catechol) is the most toxic, while the meta (resorcinol) is the least. The toxicity of phenols diminishes, while antiseptic properties increase, by the introduction of alkyl radicles in the nucleus (cresol).

If the hydroxyl groups be closed by etherification, the phenols lose their peculiar caustic and antiseptic action as with veratrole, anisole, and phenetole. That this is not the case with the safroles is due to an active double-linked side chain. In the same way the relative toxicity of the polyhydric phenols is diminished by introduction of acid radicles in place of the hydroxyl hydrogens. Thus, such esters of pyrogallol as eugallol (mono-acetate), lenigallol (tri-acetate) and saligallol (di-salicylate) are comparatively non-toxic owing to their insolubility and the slowness with which they break up when applied to a mucous surface.

If a carboxyl group is introduced into the benzene ring, an acid (benzoic) of low antiseptic power and but slight medicinal activity results, which, however, increases with the length of the side chain, as, for example, phenylacetic acid, phenylpropionic acid, and phenylbutyric acid. On the other hand, the antiseptic powers of the aliphatic acids increase with decreasing molecular weight. Whilst the entrance of chlorine in aliphatic bodies usually lends hypnotic and narcotic properties, the replace-

ment of hydrogen in the benzene nucleus by a halogen raises the antiseptic properties of the substance. No hypnotic action is discernible, since the human organism is incapable of splitting the halogen off from the nucleus. A comparative study of the relationship between chemical constitution and disinfectant action of antiseptics, by Bechhold and Ehrlich (Zeitsch. Physiol. Chem. 1906, 47, 173), has cleared up this subject in a remarkable manner. The experiments were carried out on diphtheria bacilli and other pathogenic bacteria, as *B. coli*, *pyocyaneus*, *typhi*, &c.

1. The introduction of halogens in phenol raises the disinfectant action corresponding to the number of halogen atoms (trichloro-phenol is 25 times and tribromo-phenol 45 times as active as phenol, while 1 mol. of penta-bromo-phenol is the equivalent of 500 mols. of phenol).

2. The introduction of alkyl groups in phenol and halogen phenols increases disinfectant action (tribrom-*o*-cresol is 20 times as active as tribromo-phenol; tetra-brom-*o*-cresol is in effect 250 times as active as phenol). The simple phenolic compounds and their halogen derivatives are not adapted for internal disinfection. With the introduction of a second group in the molecule toxicity is materially diminished as salicylic acid, guaiacol, &c.

3. The direct linkage of two phenols or halogen phenols through agency of a CH_2 or $CHOH$ or $CHOCH_3$ or $CHOC_2H_5$ group increases antiseptic action.

4. The union of two phenol groups through CO or SO_2 lessens disinfectant action.

5. The introduction of a COOH group into the nucleus lessens disinfectant action.

Among the disinfectants of high antiseptic power against pathogenic bacteria are:

Tetrabrom-*o*-cresol (almost non-toxic) arrests diphtheria bacilli in a dilution of 1 to 200,000 (phenol 1 to 800). In dilution of 1 to 320,000 destroys bacteria in 24 hours.

Tetrabrom-*o*-diphenol (slightly toxic), a dilution of 1 to 640,000 corresponding to 1 to 800 of phenol.

Hexabromodihydroxydiphenylcarbinol (non-toxic) dilutions of 1 to 200,000 corresponding to 1 to 800 of phenol.

The introduction of halogens into phenol depresses at first the toxicity, increasing and reaching a maximum in the penta-halogen phenol. The tri-halogen derivative is as toxic as phenol.

The introduction of the CH_3 group compensates the toxic action of halogens.

Antinosin. Nosophen sodium. See *Nosophen*.
Benzonaphthol. Benzoyl- β -naphthol

$C_6H_5 \cdot COOC_{10}H_7$ m.p. 107° – 110° , Hoechst.

Bromol. Tribromophenol, m.p. 95° , Heyden.

Bromotan. Bromtannin methylene urea, Voswinkel.

Chavosol or *Chavosote.* *p*-Allyl-phenol, dental antiseptic, Ch. Fab. Thann, Alsace.

Chinosol. Normal 8-hydroxyquinoline sulphate
 $(C_9H_7ON)_2H_2SO_4$

m.p. 175° – 177.5° (U.S. Pat. 906918), Fritzsche.
Diaphtherin or *Oxychinaseptal.* Molecular compound of 1 mol. 8-hydroxyquinoline and 1 mol. of its salt with *o*-phenolsulphonic acid

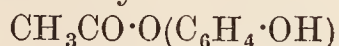
$HO \cdot C_6H_4 \cdot SO_3H \cdot (C_9H_6(OH)N)_2$

¹ Brit. Med. J.

² J. Amer. Med. Assn. 1917, 27.

³ *Ibid.* 1918, 51; 1917, 682.

Euresol. Mono-acetyl-resorcinol



Used in alopecia and seborrhea (D. R. P.P. 103857, 122145), Knoll.

Cresol preparations. As already explained, the introduction of an OH group into benzene increases its solubility, physiologic activity and antiseptic properties. Cresols are phenols in which one hydrogen atom has been replaced by CH_3 . The germicidal efficiency of phenol is thereby increased with a lowering of toxicity, hence the superiority of the cresols. Their diminished toxicity is also due to their greater dilution when used. The disadvantages of the cresols are their odour (due to impurities), variable composition (due to variation in proportions of the *o*- *m*- and *p*-cresols) and insolubility. Because of the insolubility of this antiseptic, different methods of suspending it in water have been resorted to. The most popular form of these cresols is the pharmacopœial *Liquor Cresolis Comp.*, prepared by mixing cresol with linseed oil and alcohol, and then heating with sufficient potassium hydroxide to form a clear neutral soap. This forms a clear solution with water. Various commercial preparations differ in using crude or refined cresol and other soaps. Among this class are:

Lysol (Schuelke and Mayer).

Creolin (Pearson).

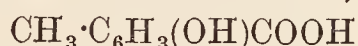
Creosapal (de Haen).

Cresolin, *cyllin* (Jeyes, London).

Sapocarbol, *solutol*.

Phenolin.

Cresols are also rendered soluble by mixing with the sodium salts of organic sulphonic acids or the alkali salts of cresotinic acid,



salicylic and other acids. As *Kresin* (Schering), *Solveol* (Heyden), *Kresulfol* (Riedel), *Sanatol* (Leonhardt), or *Cresatin*.

Cresatin. Acetic ester of *m*-cresol (U.S. Pat. 1031971), Schieffelin, N.Y.

Cretaform. Oxy-methyl-cresol-tannin.

Epicarine. β -Hydroxynaphthyl-carbinylo-hydroxy-*m*-toluic acid



(U.S. Pat. 671622, expired), m.p. 190°–195°,

Bayer.

Euguform. Acetylated methylene-diguaiacol, Hillringhaus.

Grotan. A mixture of *p*-chloro-*m*-cresol with its sodium compound, Schnellke and Mayer, Hamburg.

Hetocresol. *m*-Cresol cinnamate

m.p. 65° (D. R. P. 99567), Kalle.

Lygosins. Sodium and quinine salts of bis-*o*-hydroxybenzylideneacetone

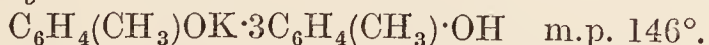


(D. R. P. 110521), Zimmer.

Nosophen. Tetra-iodo-phenolphthalein

(D. R. P. 143596), Rhenania.

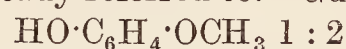
Paralysol. Solid cresol combination



Sagrotan. *p*-Chloro-*m*-cresol (66°) with chlorinated symmetrical xlenol (117°) (D. R. P. 276662), Schülke and Mayer, Hamburg.

Antiseptics, internal. This class is chiefly employed in diseases of the air passages. Apart from their antiseptic properties, the phenols

possess more or less of an analgesic and local anæsthetic effect, which, however, cannot be utilised unless substitution be resorted to in order to eliminate the caustic effect of the hydroxyl already referred to. *Guaiacol*

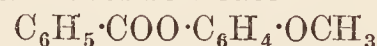


possesses in general an action similar to phenol and catechol, but is less toxic and caustic and has greater antipyretic effect. Because of its disagreeable taste and more irritant action upon the stomach compared with guaiacol, creosote has been largely replaced by the former. *Guaiacol* and its preparations excite the nervous centres, stimulating thereby the assimilative processes, also the activity of the leucocytes, elimination of the bronchial secretions and kidneys. The undesirable caustic and secondary effects of guaiacol and creosote formerly militated against their more general use until the influence of substituting groups was better understood. As has been pointed out, the toxicity of the dihydroxybenzenes depends on the presence of the free OH groups, reaching a maximum convulsive effect in catechol. If both hydroxyls are methylated, the product (*veratrole*) becomes three times less toxic than guaiacol, with, however, a disappearance of medicinal action. One hydroxyl must remain free or loosely covered if we desire to retain the specific properties of guaiacol. One method of accomplishing this is shown in the carbonic acid esters as *duotal* or *creosotal*, which are tasteless and non-irritant. Likewise carbonates of menthol, borneol, carvacrol, thymol, creosol, eugenol, &c., have been prepared. In addition, the carbamic acid esters have been prepared using chloro-carbonic amide instead of COCl_2 (D. R. PP. 11856, 116366). The easily hydrolysable organic acid esters as *benzosol*, *styracol*, &c., are perhaps more readily absorbed in the intestinal canal. Another class of derivatives with a free hydroxyl group in which the nucleus is substituted are the salts of guaiacol ortho-sulphonic acid (*thiocol*), the para derivative (*monotal*) possesses an undesirable action on the stomach. Condensation-products with formaldehyde in which two guaiacol radicles are linked by means of a methylene group (*pneumin*, *euguform*, *pulmoform*) liberate formaldehyde in minute traces. These products are quite insoluble, breaking up very slowly. Substitution in the nucleus, while yielding more soluble compounds, diminishes medicinal activity. Patents have been taken (D. R. P. 258473) in which the sulphonic acid rest has been introduced in the side chain (alkyl) group of guaiacol. Patents protect the alkali salts of catechol ether-oxy-propane-sulphonic acid. Wolff, Hamburg.

Since phosphites are useful in treating tuberculosis, guaiacol phosphite, *phosphatol* $\text{P}(\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{OCH}_3)_3$ and creosote-phosphite have been prepared (D. R. P. 95578).

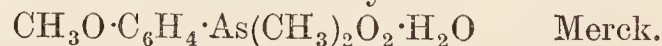
Aethacol (*thanatol*). Catechol monoethyl ether b.p. 210°, Kalle.

Benzosol. Guaiacol benzoate



m.p. 60° (U.S. Pat. 453035), Hoechst.

Cacodyliacol. Guaiacol cacodylate



Cetiacol (*Palmiacol*) catechol methyl cetyl ether (Br. Med. J. 1897, 137).

Creosol. One of the most valuable therapeutic constituents of creosote obtained by methylating homocatechol (D. R. P. 258105), Fahlberg, Litz, Westerhausen.

Creosotal. Creosote carbonate (U.S. Pat. Exp. 501235), sp.gr. 1.145 to 1.17.

Cresoform. Condensation product of formaldehyde and creosote.

Duotal. Guaiacol carbonate (D. R. P. 58129), Bayer.

Eosote. Creosote valerate, b.p. 81°–85° (3 mm.), Lehmann.

Etelen. Triacetyl gallic acid ethyl ester, Bayer.

Eucol. Guaiacol acetate
 $\text{CH}_3\text{OC}_6\text{H}_4\text{OOC}\cdot\text{CH}_3$

b.p. 235°–240°, C. Erba, Milan.

Euguform. Acetylated condensation product of guaiacol and formaldehyde, Hillringhaus.

Geosote. Guaiacol valerate

$\text{CH}_3\text{O}\cdot\text{C}_6\text{H}_4\text{OOC}\cdot\text{C}_4\text{H}_9$ b.p. 260°, Lehmann.

Guaiacetin. *o*-Hydroxyphenyl ether of sodium glycollate

$\text{HO}\cdot\text{C}_6\text{H}_4\text{O}\cdot\text{CH}_2\text{COONa}$

m.p. 130°, Van Gember.

Guacamphol. Guaiacol camphoric ester

$\text{C}_8\text{H}_{14}(\text{COO}\cdot\text{C}_6\text{H}_4\cdot\text{OCH}_3)_2$

m.p. 126°, Henning.

Guaiachinol. Quinine dibromoguaiacolate

$\text{C}_6\text{H}_2\text{Br}_2(\text{OCH}_3)\text{OH}\cdot\text{Q}$

Guaiaperol. Molecular compound of guaiacol and piperidine

$\text{C}_5\text{H}_{11}\text{N}\cdot(\text{HOC}_6\text{H}_4\text{OCH}_3)_2$ m.p. 80°.

Guaiacyl. Calcium orthoguaiacol sulphonate (local anæsthetic)

$(\text{C}_6\text{H}_3(\text{OH})(\text{OCH}_3)\text{SO}_3)_2\text{Ca}$

Guaiiform. *Geoform.* Condensation product of guaiacol and formaldehyde, Henning.

Guaiamar. Glycerol ether of guaiacol

$\text{CH}_3\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{OCH}_2\cdot\text{CHOH}\cdot\text{CH}_2\text{OH}$

m.p. 75° (U.S. Pat. 599125), Mkd't.

Guaiasanol. Diethylglycyl guaiacol hydrochloride

$\text{CH}_3\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{N}(\text{C}_2\text{H}_5)_2\cdot\text{HCl}$

m.p. 183° (U.S. Pat. 624772), Hoechst.

Guaiacol carbonate (Duotal)

$(\text{CH}_3\text{OC}_6\text{H}_4\text{O}_2)_2\text{CO}$

m.p. 83 to 87.

Guatannin. Guaiacol-tanno-cinnamate (D. R. P. 133299), Berlin Lab.

Hexamecoll. A condensation product of hexamethylene-tetramine and guaiacol. Used externally.

Kreosal. Creosote tannate.

Monotal. Methoxyacetyl guaiacol

$\text{CH}_3\text{O}\cdot\text{CH}_2\text{COO}\cdot\text{C}_6\text{H}_4\cdot\text{OCH}_3$

b.p. 156° (15 mm.) (U.S. Pat. 822339), Bayer.

Pneumin. Methylene creosote (cond.-prod. formaldehyde and creosote), Speier.

Phosote. Creosote phosphate, b.p. 190°–203°.

Pulmoform. Methylene guaiacol. See *Pneumin.* Speier.

Resaldol. Ethyl ester of 2:4-dihydroxybenzoyl-*o*-benzoic acid

$(\text{OH})_2\text{C}_6\text{H}_3\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{COOC}_2\text{H}_5$ Bayer.

Salocreol. Creosote salicylate, Heyden.

Styracol. Guaiacol cinnamate, m.p. 130° (D. R. P. 62176), Knoll.

Tanno-cresoform and *guaiiform.* Comp. of

creosote or guaiacol with tannin by aid of formaldehyde.

Taphosote. Tannophosphate of creosote, Lambiotte Fr., Paris.

Thiocol. Guaiacol sulphonate of potassium

$\text{C}_6\text{H}_3(\text{OH})(\text{OCH}_3)(\text{SO}_3\text{K})$, 1:2:6

(U.S. Pat. 650218, exp.), La Roche.

Trimethol. Tri-methyl-methoxy-phenol

$\text{C}_6\text{H}(\text{CH}_3)_3(\text{OCH}_3)\text{OH}$

Leeming Walker Lab., N.Y.

Thymatol. Thymol carbonate

$(\text{CH}_3\cdot\text{C}_6\text{H}_3(\text{C}_3\text{H}_7)\text{O}_2)_2\text{CO}$

Intestinal antiseptics. These compounds are intended to break up only under the influence of the alkaline intestinal secretions. Intestinal asepsis is unattainable, nevertheless numerous combinations serve valuable purposes in securing partial disinfection, inhibiting the development of milder types of bacteria, neutralising the action of toxins and arresting disturbing fermentative action in the canal. The many organic bismuth compounds serve in this capacity (as marcasol, thioform, iodylin, &c.), also various phenol esters of salicylic acid as salol, also guaiacol esters, naphthyl esters (alpol and betol).

Alpol. α -Naphthyl salicylate, m.p. 83°.

Benzonaphthol. β -naphthyl benzoate

$\text{C}_6\text{H}_5\cdot\text{COOC}_{10}\text{H}_7$

m.p. 107°–110°.

Betol. β -Naphthyl salicylate, m.p. 95°.

Chinaphthol. β -Naphthyl monosulphonate of quinine, m.p. 185°, Merck.

Eugenoform. Eugenol carbinol sodium, m.p. 160°.

Isoform. *p*-Iodoxyanisole $\text{CH}_3\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{IO}_2$ (D. R. P. 161725), Hoechst.

Kresalol. *m*-Cresol salicylate

$\text{CH}_3\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{OC}\cdot\text{C}_6\text{H}_4\cdot\text{OH}$ m.p. 74°.

Microcidin. Sodium beta-naphthol.

Resaldol. See previous section on internal antiseptics.

Salacetol. Hydroxy-acetone salicylate

$\text{HO}\cdot\text{C}_6\text{H}_4\cdot\text{COO}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}_3$

m.p. 71°, Schoetensack.

Salithymol. Salicylic thymyl ester

$\text{CH}_3\cdot\text{C}_6\text{H}_3(\text{C}_3\text{H}_7)\text{O}\cdot\text{COC}_6\text{H}_4\cdot\text{OH}$

Thymacetol. A condensation product of acetone and *o*-thymic acid.

Lactol. β -Naphthyl lactate

$\text{CH}_3\cdot\text{CH}(\text{OH})\text{COO}\cdot\text{C}_{10}\text{H}_7$

Tribromo-beta-naphthol, Chem. Fab. Ladenburg, Baden.

Intestinal astringents. These consist chiefly of condensation-products or similar compounds of tannin with formaldehyde or hexamethylene-tetramine. In order to secure their astringent and other medicinal effects upon the intestinal mucous surface for relieving inflammatory conditions and retarding bacterial action, such combinations are intended to pass through the stomach unchanged and break up into their constituent parts under the influence of the alkaline secretions. They are chiefly employed in catarrhal and inflammatory conditions as dysentery, tubercular diarrhoea, cholera, &c.

Cretaform. Oxymethylene tannin.

Gallogen. Egallic acid (D. R. P. 137033-4), Heinemann.
Honthin. Keratinised tannin albuminate, Hell Co.
Rexotan. Methylene-tannin-urea, Voswinkel.
Tanargan. Tannin silver albuminate, Weil.
Tannalbin. Tannin albuminate (U.S. Pat. 563479), Knoll.
Tannin albuminate. Formerly Tannalbin, Merck.
Tannigen. Diacetyl-tannin (U.S. Pat. 533718), Bayer.
Tannisol. Methylene-ditannin, Wolfrum.
Tannocasum. Casein tannate.
Tannoform. Methylene-ditannin, m.p. 230° $\text{CH}_2(\text{C}_{14}\text{H}_9\text{O}_9)_2$ (D. R. P. 88841), Merck.
Tannopin (tannon). Hexamethylenetetramine tannin $(\text{CH}_2)_6\text{N}_4(\text{C}_{14}\text{H}_{10}\text{O}_9)_3$ (U.S. Pat. 607172), Bayer.
Tannothymal. Condensation product of formaldehyde, thymol and tannin (D. R. P. 188318), Schimmel Co.
Tannyl. Tannin oxychloro-casein, Gehe Co.
Tanocol. Tannin gelatin comp., Agfa.

DIURETICS AND DIATHETICS.

These remedies are employed, more especially, in treatment of rheumatism, gout, lithiasis, and various forms of uric acid diathesis. They may be classified according to the manner of action and objects sought.

(a) To diminish the formation of uric acid through the use of quinic acid



combinations such as urol, new sidonal or combinations of it with lithium (Urosin) or piperazine (Sidonal).

(b) To retard the deposition of uric acid through the solvent action of salts of organic amine bases such as piperazine, lycetol, &c.

(c) To produce profuse diuresis and thereby through flushing, eliminate the urates. To this class belong the purine derivatives such as theophylline and those of phenylcinchonic acid such as atophan.

(a) **Quinic acid combinations.** The important members of this group are combinations of quinic acid with members of group (b).

Chinotropin. Urotropin quinate, Schering.

New Sidonal. A mixture of quinic anhydride and quinic acid, Charlottenburg.

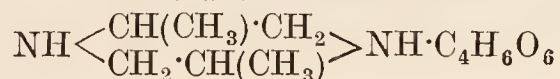
Sidonal. Piperazine quinate (Eng. Pat. 11420; U.S. Pat. 665879, expired), m.p. 168°-171°, Charlottenburg.

Urol. Urea quinate, m.p. 106° (D. R. P. 124426), Schulz.

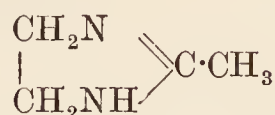
(b) **Ethylene-amines and derivatives.** Of this class, ethylene-diamine exerts a solvent action on false membranes and even coagulated protein, while the others of the piperazine class possess a remarkable solvent action on urates in addition to a diuretic action. Experimentally it has been shown that acid sodium urate is soluble 1 in 1150 of water, while the piperazine compound is 1 in 50, and the lysidine salt 1 in 6.

Ethylene-diamine, $\text{NH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}_2$, Schering.

Lycetol. Dimethylpiperazine tartrate, m.p. 250°



Lysidin. A 50 p.c. sol. of 2-methyl-4:5-dihydroglyoxaline



m.p. 105°-106° (U.S. Pat. 523018, expired), Bayer, Hoechst.

Piperazine. Diethylene-diamine



m.p. 104°, b.p. 145° (U.S. Pat. 543214, expired), Bayer.

Sidonal. See under Quinic acid, above.

Solurool. A thymic acid preparation from thymus gland (D. R. P. 104908), the decomposition products of which are related to piperazine.

(c) **The purine and phenylcinchonic acid derivatives.** These two popular classes of diuretics serve through profuse diuresis to prevent uric acid deposition rather than its formation.

In the past, lithium salts, in addition to the alkali citrates and benzoates, were extensively used on the assumption of the conversion of the insoluble acid urates into soluble salts, through interaction, which were then eliminated through profuse diuresis.

Lithium salts are open to the objection that they not only fail to form soluble urates, but also produce secondary effects on the nervous system.

The alkali citrates, benzoates, acetates, and formates are usually employed in conjunction with the purine derivatives as soluble double salts.

The purine derivatives. Qualitatively, the diuretic action of the methylated purine derivatives corresponds to their influence upon the muscular system, while the reverse is noted in their exciting action on the central nervous system. That is, the stronger the effect of a purine derivative upon the muscular system, the more marked is its diuretic action and the less its influence upon the nervous system. The effect of theobromine on the nervous system is far weaker than that of caffeine, while its diuretic action is equally strong. The relative diuretic action of this class of derivatives depends upon the positions methylated, thus the positions 1:3 (theophylline) and 1:7 (paraxanthine) are of greater pharmacological importance than 3:7 (theobromine). Trimethylxanthine (caffeine), while possessing a slight diuretic action, exerts a too powerful influence upon the brain for diuretic purposes (Archiv Exp. Path. u. Pharmacologie, 1900, 319).

Theobromine and theophylline excel in diuretic, cardiac, and muscular actions since they are more effective and prompt, also almost free from such secondary effects as insomnia, nervousness and gastric disturbances. This applies especially to theobromine. Theophylline excels the latter in diuretic efficiency.

The introduction of ethyl groups in place of methyl, produces no material change in action. The objectionable slow action of the methylated xanthines, due to their insolubility, is relieved by necessary combination with organic salts of the alkalis (sodium salicylate, benzoate, acetate, formate) in the form of double salts.

Caffeine derivatives. *Symphorol.* Various

alkali salts of caffeine sulphonic acid. With the introduction of sulphonic acid, caffeine loses its effect on the vasomotor centre, while its diuretic action is retained. The acyl-amino derivatives of caffeine possess a strong diuretic action without the secondary effects of caffeine, for example, the mono- and diacetyl-amino-caffeine (D. R. P. 139960).

Hetol: Caffeine sodium cinnamate (Kalle).

Dimethyl-xanthines. *Theobromine* (*santose*), 3 : 7 dimethylxanthine.

Agurin. Theobromine sodium-sodium acetate, Bayer.

Barutin „ barium-sodium salicylate, Agfa.

Diuretin „ sodium salicylate, Knoll.

Theobromose „ lithium.

Theocylene. Condensation-product of aspirin and theobromine.

Theophorin. Theobromine sodium-sodium formate (U.S. Pat. 799764), La Roche.

Theolactin. Theobromine sodium-sodium lactate, Zimmer.

Urocitral. Theobromine sodium-sodium citrate, Rump.

Uropherin B and S. Theobromine lithium benzoate and salicylate, Merck.

Theophyllin (*theocin*) synthetic 1 : 3-dimethyl-xanthine, m.p. 268° (D. R. P. 138444; U.S. Pat. 757328-9),¹ Bayer, Boehringer.

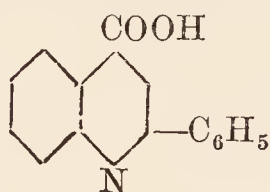
Theophyllin (*theocin*) sodium acetate



(U.S. Pats. 667381, 757325-9, expired), Bayer, Merck.

Euphyllin. Theocin ethylene-diamine, Byk.

2. Phenylcinchoninic acid derivatives. 2-Phenylquinoline 4-carboxylic acid



(D. R. P. 267208) and its various esters have been found to give excellent results in treatment of acute gout, sciatica, articular rheumatism, &c., through stimulating the kidneys. They also serve as urinary disinfectants and possess in addition analgesic properties. Most successful among these are :

Atophan. (Phenyl-cinchoninic acid, U.S. P.), 2-phenylquinoline 4-carboxylic acid



m.p. about 210° (U.S. Pat. 1075171), Schering.

Acitrin. The ethyl ester of atophan or 2-phenylquinoline 4-carboxylic ethyl ester



m.p. 61°, Bayer.

Hexophan. Oxyphenyl-quinoline dicarboxylic acid, Hoechst.

Novatophan. The methyl derivative of acitrin or 6-methyl-2-phenyl-quinoline 4-carboxylic ethyl ester



m.p. 76° (U.S. Pat. 1045759), Schering.

¹ Synthesis, Ber. 1900, 33, 3053.

Paratophan. 6-Methyl-2-phenylquinoline 4-carboxylic acid, Schering.

Phenylcinchoninic acid. U.S. P. title for atophan.

Isatophan. Methoxy-phenyl-quinoline carboxylic acid, m.p. 216°.

Iriphan or *Triphan*. The strontium salt of atophan, Wolff, Elberfeld.

Synthalin. Methyl ester of piperonyl-atrophan, m.p. 134°-135°, Bayer.

Diaphthol (*chinaseptol*) o-hydroxy-quinoline-m-sulphonic acid $C_9H_5N(OH)SO_3H$, m.p. 295°.

URINARY ANTISEPTICS.

Hexamethylene-tetramine, Hexamethyleneamine (U.S. P.), the representative of this very popular class of remedies, of which there are a great variety of combinations, splits up in acid fluids with liberation of nascent formaldehyde. Hence their value as active urinary antiseptics in treatment of various infections of the urinary passages so long as the urine is not secreted in an alkaline state. In contact with tissues and secretions which are either neutral or slightly alkaline, no reaction takes place. The various combinations of hexamethyleneamine represent the medicinal properties of this base in conjunction with those of the combining acid or compound.

Hexamethylene-tetramine $(CH_2)_6N_4$, which boils at 263°, is used under such titles as *Cystamine*, *Cystogen*, *Urotropin*, *Hexamine*, *Formin*, *Aminoform*, &c.

Amphotropin. Hexamethyleneamine camphorate $[(CH_2)_6N_4]_2 \cdot C_8H_{14}(COOH)_2$, a molecular compound of 1 mol. camphoric acid and 2 mol. hexamethylene-tetramine (U.S. Pat. 1064227; D. R. P. 270180), Hoechst.

Borovertin. Hexamethylene-tetramine tri-borate $(CH_2)_6N_4 \cdot 3H_3BO_3$ (D. R. P. 188815), Agfa.

Chromoform. Hexamethylene-tetramine methyl dichromate $(C_6H_{12}N_4)(CH_3)_2Cr_2O_7$, K. Schmitz, Breslau.

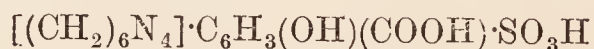
Cystopurin. Double salt of one mol. hexamethylene-tetramine and two of sodium acetate, Wuelfing.

Similar salts with sodium citrate and benzoate are known respectively as *Formurol* and *Cystazol*, Henning.

Galloformin. Compound of hexamethylene-tetramine and gallic acid, Henning.

Helmitol. Hexamethylene-tetramine methylene citrate $C_7H_8O_7[(CH_2)_6N_4]$, m.p. 165°-175° (U.S. Pat. 722275), Bayer.

Hexal or *Hexalet*. Hexamethylene-tetramine salicyl-sulphonate



(D. R. PP. 266122-3), Riedel.

Hetratin. Resorcinol hexamethylene-tetramine $C_6H_6O_2[(CH_2)_6N_4]$.

Neohexal Secondary sulphasalicylate of hexamethylene-tetramine, soluble (D. R. PP. 240612, 266122), Riedel.

Rhodaform. Claimed to be a compound of the methyl ester of sulphocyanic acid and hexamethylene-tetramine (D. R. PP. 266788, 269746, 270486, 275092), H. Schmitz, Breslau.

New compounds of $(CH_2)_6N_4$ with metal salts

of nucleic acid (D. R. P. Anm. P. 32108), Gans.

ANÆSTHETICS.

We distinguish between products that produce (1) total anæsthesia and (2) local anæsthesia.

Total anæsthetics (by inhalation). This class belongs exclusively to the aliphatic series and depends largely, for its action, upon the presence of chlorine, intensity in action increasing with the number of chlorine atoms introduced; thus CH_3Cl is feebly narcotic, while CCl_4 paralyses the heart. The corresponding bromine derivatives also possess a narcotic effect, but because of their intense action only the ethyl bromide and bromoform are employed, and these internally. Such members of the alkyl halides as have a very low boiling-point, are employed as local anæsthetics by freezing. For the preservation of anæsthetic ether, see Middleton (Pharm. J. 1924, 113, 98). For the examination of carbon tetrachloride for medicinal purposes, see Perkins (Pharm. J. 1924, 113, 101). For the quantitative determination of carbon disulphide in carbon tetrachloride, see Perkins (Pharm. J. 1924, 113, 102). No improvement over chloroform or ether has appeared, although some of this group serve in certain specific cases (see introduction *Hydrocarbons*). More prominent are:

Ethyl chloride $\text{C}_2\text{H}_5\text{Cl}$, b.p. $+12^\circ$. Used as inhalant and also as a local anæsthetic.

Ethyl iodide $\text{C}_2\text{H}_5\text{I}$, b.p. 72° . Inhaled for asthma.

Ethyl bromide $\text{C}_2\text{H}_5\text{Br}$, b.p. 37° – 39° . Total anæsthetic, rapid and short duration.

Ethylene has been recently recommended instead of nitrous oxide. See introduction *Hydrocarbons*.

Ethylene chloride $\text{C}_2\text{H}_4\text{Cl}_2$, b.p. 83° . Inhalation and local anæsthetic.

Ethylene bromide $\text{C}_2\text{H}_4\text{Br}_2$, b.p. 130° . Internally in epilepsy.

Ethylidene chloride $\text{CH}_3\cdot\text{CHCl}_2$, b.p. 58° – 60° . Anæsthetic.

Kelene. Commercial name for a special brand of ethyl chloride.

Methyl chloride CH_3Cl , b.p. -22° . If evaporation be accelerated by a current of air a temperature of -55° may be obtained. Local anæsthetic.

Methylene chloride CH_2Cl_2 , b.p. 42° . Inhalation and local anæsthetic.

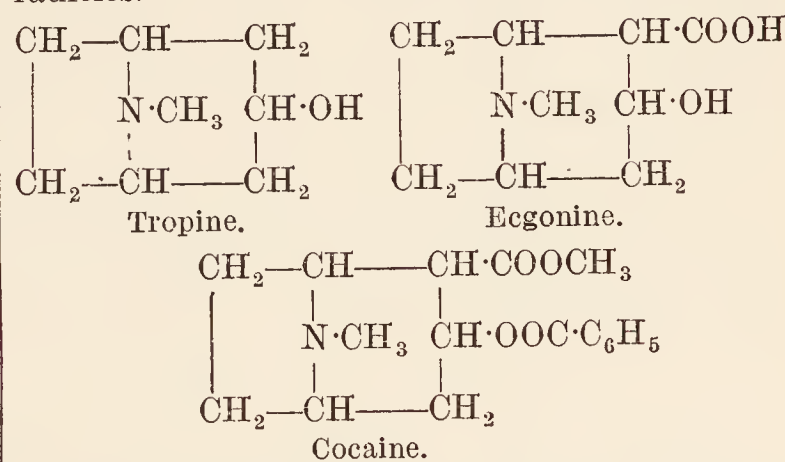
Somnoform. A mixture of ethyl chloride 60 parts, methyl chloride 35 parts, and ethyl bromide 5 parts. Anæsthetic.

Pental, tri-methyl-ethylene $(\text{CH}_3)_2\text{C}:\text{CH}\cdot\text{CH}_3$, b.p. 38° . Dental anæsthetic.

Local anæsthetics. These drugs may be divided into two classes: (1) those which produce local anæsthesia through the production of cold, due to rapid vaporisation such as ethyl and methyl chlorides, ethylene chloride, and pental. These are given under total anæsthetics for convenience; (2) such local anæsthetics as have a specific effect on the sensory nerves or their terminals such as members of the cocaine class. Cocaine, introduced as local anæsthetic in 1885 by Koller, still retains its popularity because of its intensity and depth of action. Objectionable features are its irritant effects and dilatation of

the pupil in eye practice, hydrolytic decomposition through standing of its aqueous solutions or sterilisation, and excitation and paralysis of the central nervous system. Attempts have been made to find a substance possessing the virtues of cocaine stable in solution and free as possible from untoward secondary effects. Partial success has been attained, all the compounds are designated stable to sterilisation, and in general, each is specially adopted for certain lines of local anæsthesia.

Modern developments in local anæsthetics are due to the elucidation of the constitution of cocaine by Liebermann, Ladenburg, Einhorn, and particularly by Willstätter. On hydrolysis cocaine yields ecgonine, which is tropine carboxylic acid (tropine being formed by the hydrolysis of atropine). Ecgonine may be regarded as resulting from the fusion of a piperidine with a pyrrolidine ring. In cocaine the hydroxyl of ecgonine is esterified with benzoic acid, the carboxyl with methyl alcohol. If either or both ester groupings are hydrolysed there is no anæsthetic action. The replacement of methyl by other alkyls yields homologues which differ but slightly quantitatively. If other aromatic acid radicles replace the benzoyl group, anæsthetic action is materially lessened or disappears. For example,¹ truxilline (isotropyl-cocaine), valeryl-cocaine, and phenylacetyl-cocaine hydrochlorides possess but little if any local anæsthetic action, while they exhibit a toxic effect on the liver. These bodies differ from cocaine in that the benzoyl group is replaced by the above acid radicles.



The Java coca leaf contains an alkaloid called tropa-cocaine, which is more active than cocaine, less toxic and more stable; it is the benzoyl ester of pseudo-tropine, differing from tropine only in its stereo-configuration, and is without mydriatic action.

Tropeins obtained from tropine (as, for example, tropine with tropic acid (α -phenyl-hydracrylic acid) yields atropine), possess a marked mydriatic with weak local anæsthetic action, while stereoisomers derived from pseudo-tropine are devoid of mydriatic and possess a strong local anæsthetic action.

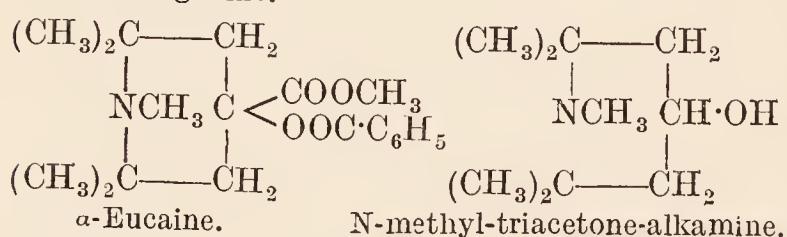
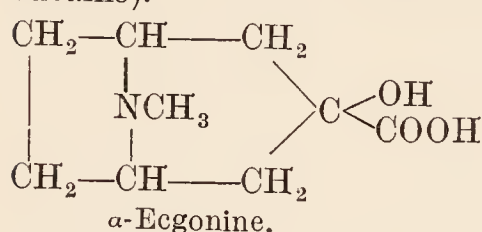
The general conclusions drawn from this are: that the action of cocaine is dependent upon the presence of a nitrogenous nucleus, an esterified carboxyl (COOR), and a benzoyl group.² On these assumptions the search for ideal local anæsthetics has progressed in two directions; namely, derivatives containing a cyclic nitrogen

¹ Ber. 21, 2347; Deutsche Med. W. 32, 717.

² References to the mydriatic action of cocaine are made under the mydriatics.

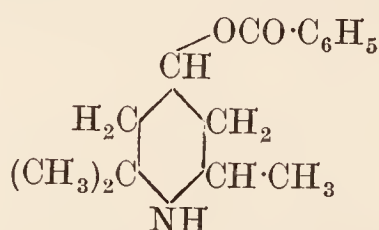
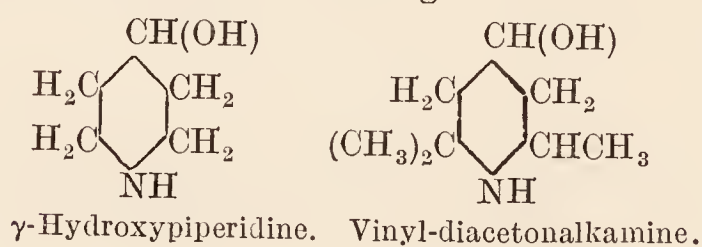
and the amino- and oxyamino-benzoic alkyl esters.

The chief objects in the preparation of these derivatives have been to find bodies less toxic, more stable (to sterilisation), and less irritating to the tissues than cocaine. Most of these new derivatives possess the undesirable effect of dilating the blood vessels, not constricting them as cocaine, hence these bodies are usually employed in conjunction with epinephrine. From tropinone (ketone corresponding to tropine), through treatment with HCN and subsequent hydrolysis, α -ecgonine is obtained. This differs from ecgonine in that the carboxyl and OH groups are united to the same carbon. From this by benzylation and methylation, α -cocaine is obtained, which is devoid of local anæsthetic action; however, a similar α -derivative of N-methyl-acetone-alkamine possesses marked local anæsthetic action (α -eucaine).¹



This α -eucaine, which is less toxic and more stable than cocaine, was found to be irritating when injected, hence was superseded by β -eucaine,² the hydrochloride of benzoyl-vinyl-diacetone-alkamine which contains the piperidine ring of cocaine.

β -Eucaine, used chiefly in the form of lactate (m.p. 155°) or hydrochloride (m.p. 268°) in 2 to 3 p.c. solutions (D. R. PP. 90069, 97672). (*Benzaminae Lactas*, B.P.). Not adapted for lumbar anæsthesia. Schering.

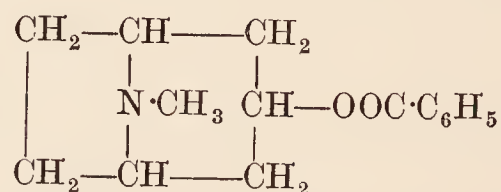


β -Eucaine, O-benzoyl- α -vinyl-diacetonalkamine.

The name iso - β -eucaine is proposed for the O-benzoyl derivative of β -vinyl-diacetonalkamine. (α - and β -Vinyl-diacetonalkamines are diastereoisomeric, and hence β -eucaine and iso - β -eucaine are similarly related.) β -Eucaine has been resolved by means of camphorsulphonic acid and iso - β -eucaine by means of bromo-camphorsulphonic acid. On the rabbit's cornea β -eucaine, iso - β -eucaine, and their optically

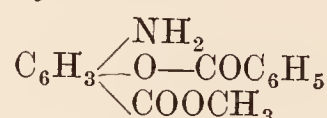
active components have approximately equal local anæsthetic action; on the sciatic nerve of the frog, however, β -eucaine is a more powerful anæsthetic than iso - β -eucaine. The relative toxicity of the various bases, determined on mice by subcutaneous injection and expressed in mg. per 1 gram. of mouse, is as follows: r - β -eucaine, 0.8–0.9; d - β -eucaine, 1.5; l - β -eucaine, 0.6–0.7; r - iso - β -eucaine, d - iso - β -eucaine, and l - iso - β -eucaine, 0.5 (H. King, J. Chem. Soc. 1924, 125, 41; J. Soc. Chem. Ind. 1924, 43 B, 276).

Tropa-cocaine.—The hydrochloride of benzoyl-pseudo-tropine, a stereoisomeride of tropine, found in the Javanese coca leaf, also prepared synthetically.³ Used like cocaine and is only $\frac{1}{4}$ to $\frac{1}{3}$ as toxic; m.p. 271° (U.S. Pat. 628293), Merck.



Attempts involving the utilisation of the pyrrolidine ring of the ecgonine molecule were next made, but these were soon confined to benzene derivatives, since a number of well-known bodies, as creosote, eugenol, &c., belonging to this nucleus, possessed local anæsthetic properties.

Selecting a compound of a constitution analogous to that of cocaine, containing nitrogen, a benzoyl and an esterified carboxyl group, namely, methyl benzoxy-amino-benzoate



in accordance with theory, a local anæsthetic was produced. Subsequent experiments demonstrated that the benzoyl group was superfluous, since a benzene ring was already present, also the benzoyl-free compound possessed a more marked anæsthetic action. The phenol hydroxyl was found not to be absolutely essential, although its presence bestowed antiseptic properties.

These experiments, made in 1897 by Einhorn and Heinz,⁴ demonstrated that the esters of aromatic, amino and hydroxyamino acids possessed, in general, local anæsthetic properties. See for a general survey a lecture by Pyman, J. Chem. Soc. 1917, 111, 1117.

The first of this group to be introduced was:

Orthoform, methyl p -amino- m -hydroxybenzoate, m.p. 120°–121°. A cheaper isomeride followed in—

Orthoform new, methyl m -amino- p -hydroxybenzoate, $\text{C}_6\text{H}_3(\text{COOCH}_3)(\text{NH}_2)(\text{OH})$ 1:3:4, m.p. 142°. Because of their insolubility, these are used dry. The acid soluble salts are irritating and frequently produce necrosis. (D. R. PP. 97333–4, 111932; U.S. Pats. 610348, 625158, expired), Hoechst.

Simple alterations in the above formulæ produced—

³ Willstätter, Ber. 1896, 29, 936; Willstätter and Iglaue, Ber. 1900, 33, 1710; Barrowcliff and Tutin, Chem. Soc. Journ. 1909, 95, 1966.

⁴ Virchow's Archiv. 1896, 145, 78; 1897, 149, 217; 1898, 154, 547; Annalen der Chemie, 311, 26, 154; 325, 305, 359, 145; 371, 125, 131, 142, 162.

¹ Ber. Deuts. Pharm. Ges. 1897, 173.

² Annalen, 1897, 328; 1898, 346; Eng. Pat. 101738.

Anæsthesin, ethyl *p*-aminobenzoate



m.p. 90° – 91° (D. R. P. 19416 K.). Used locally, especially internally in hyperæsthesia of stomach, gastralgia, excessive vomiting, &c. No secondary effects as yet observed. The hydrochloride of anæsthesin is used hypodermically in 1 to 4 p.c. solutions. Hoechst.

Cycloform, *p*-amino-benzoic *iso*-butyl ester



m.p. 65° (U.S. Pat. 958110). Bayer.

Propæsin, *p*-amino-benzoic propyl ester



m.p. 73° . Like anæsthesin, it is non-irritant and non-toxic for internal and local uses. (U.S. Pat. 950936). Fritzsche.

Subcutin (soluble anæsthesin) anæsthesin *p*-phenolsulphonate



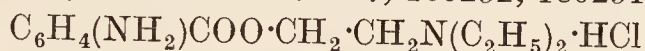
m.p. 195.6° . Ritsert.

In the endeavour to produce a substance related to orthoform, soluble in water with neutral reaction and adapted for subcutaneous use, the following resulted:—

Nirvanin,¹ Diethyl-glycylamino-salicylic methyl ester

$\text{C}_6\text{H}_3(\text{OH})(\text{COOCH}_3) \cdot \text{NH} \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{N}(\text{C}_2\text{H}_5)_2$ 1:2:4
m.p. 185° . Used chiefly in dental and eye practice; less toxic but less penetrating than cocaine. Hoechst.

Novocaine or *Procaine*, hydrochloride of *p*-aminobenzoyl- β -diethylamino-ethanol (U.S. Pat. 812554; D. R. PP. 179627, 180292, 180291)



m.p. 156° . This is a diethylamino-ethyl alcohol derivative of anæsthesin, m.p. 155° . Used in conjunction with adrenaline, toxic effects only noticed in lumbar anæsthesia. Claimed to be $\frac{1}{6}$ as toxic as cocaine. Hoechst.

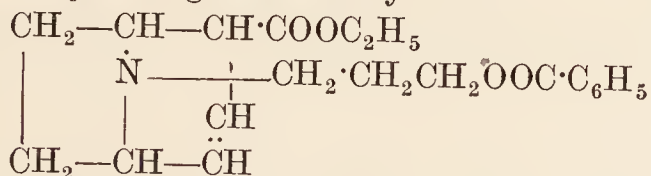
For a homologue of novocaine which promises to be useful in eye-practice, see Bonar and Sollmann (J. Pharm. exp. Therap. 1922, 18, 467). It is *p*-aminobenzoyl-dinormalbutylamino-propanol; the ethanol derivative is not so good.

For benzoylated amino alcohols of the type $\text{NMe}_2 \cdot \text{CH}_2 \cdot \text{CMeR} \cdot \text{OH}$ and



where R is aliphatic or aromatic, see Launoy and Fujimori (Compt. rend. Soc. Biol. 1919, 82, 732).

Ekkain (von Braun and Müller, Ber. 1918, 51, 251; D. R. P. 301139) is N-benzoxypopyl-noranhdydro-ecgonidine ethyl ester

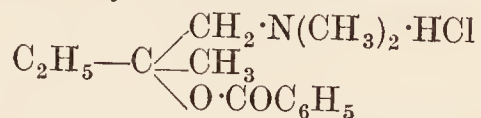


To some extent it combines the structure of cocaine with that of novocaine.

In some of the more recent introductions, the amino group has been transferred to the side chain, yielding compounds which represent substituted tertiary alcohols. The dimethyl-amino groups have a very important bearing on the physiological action of these compounds.

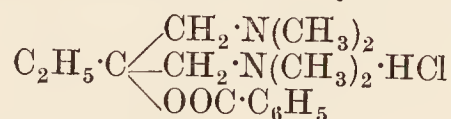
¹ Münchener med. W. 1898, D. R. PP. 106502, 108027, 108871.

Stovaine, 2-benzoxo-2-methyl-1-dimethyl-aminobutane hydrochloride



m.p. 175° : should not be sterilised above 115° . About $\frac{1}{3}$ as toxic as cocaine, used in $\frac{1}{2}$ to 1 p.c. solutions as a general all-round local anæsthetic, but especially in spinal anæsthesia (U.S. Pat. 829262, 829374). Poulenc Frères.

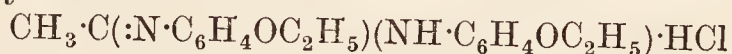
Alypin, hydrochloride of 2-benzoxo-2-dimethylamino-methyl-1-dimethyl-amino-butane



m.p. 169° ; sterilisable. Alypin is the dimethyl-amino derivative of stovaine. Used in spinal anæsthesia, also as a non-toxic general local anæsthetic like cocaine. Does not produce mydriasis (U.S. Pat. 808748). Bayer.

A slight local anæsthesia was noticed while experimenting with the aniline antipyretics, formanilide being stronger than acetanilide. By the addition of a second basic group to phenetidine derivatives, marked anæsthetic action is developed. To this class belong:

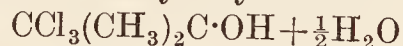
Holocaine, di-(*p*-ethoxyphenyl)acetamidine hydrochloride



m.p. 189° . Used only in eye practice. Too toxic for subcutaneous use (D. R. P. 80568). Hoechst.

Acoin, di-*p*-anisyl-mono-*p*-phenetylguanidine $\text{C} : (\text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{OC}_2\text{H}_5)(\text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{OCH}_3)_2 \cdot \text{HCl}$, m.p. 176° . Used in eye practice and dentistry. Strong solutions cause irritation. No toxic effects from weaker solutions: less toxic than cocaine. V. Heyden.

Chlorbutanol or *Chloretone*, acetone chloroform, trichlorotertiarybutyl alcohol



m.p. 96° – 97° . The 1 p.c. aqueous solution sold under the name of anesin (aneson). Employed as local anæsthetic in conjunction with cocaine and adrenaline. Parke Davis.

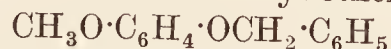
Methaform. See *Chlorbutanol*.

Aposthesine. Cinnamic ester of gamma-diethyl-amino-propyl alcohol, HCl, m.p. 137° . Parke Davis.

Dr. D. I. Macht of Johns Hopkins University introduced benzyl alcohol as a local anæsthetic, used by injection and on mucous surfaces in 1 to 4 p.c. solution, being non-irritating and non-toxic. Various benzyl esters are under clinical experimentation.

Benzyl alcohol, $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$, b.p. 200° to 206° .

Benzcain. Guaiacol benzyl ether



diethylamino-acetic menthyl ester (Hoechst, D. R. P. 261228), glycoll menthyl ester and *o*-thymotin bi-acid-acetal ester (D. R. P. 258936), possess local anæsthetic action.

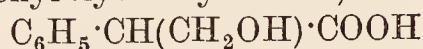
Mydriatics. Atropine and cocaine are closely related chemically and in some respects pharmacologically; cf. the section on local anæsthetics above.

Atropine is an ester which on hydrolysis yields an optically inactive tropic acid.²

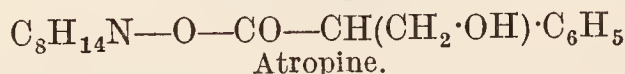
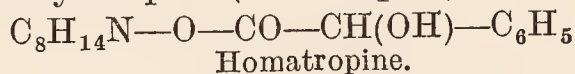
² Annalen, 148, 236.

Hyoscyamine (from belladonna) is an ester of tropine with lævo-tropic acid,¹ hence atropine must be a racemic form of hyoscyamine. Dextro-hyoscyamine is obtained from tropine and dextro-tropic acid.² In action, atropine is intermediate between that of the two other optically active forms.³

In both atropine and cocaine the hydroxyl group is esterified by an aromatic acid, tropic acid (α -phenyl-hydracrylic acid)

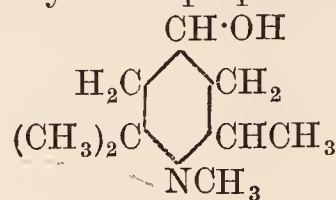


serving in atropine, and benzoic acid in cocaine, in addition to the methyl group attached to the carboxyl. Both atropine and cocaine influence alike the central nervous system, first as excitants, then paralysing; they also exert a paralysing influence on the peripheral terminals of certain nerves, whilst cocaine exerts this effect particularly on the sensory nerve terminals, the action of atropine is manifold in other directions. Mydriatically, both alkaloids are alike; cocaine, while producing a less marked dilatation of the pupil, has a more prolonged effect. The basic nuclei of these alkaloids occasion a paralysing effect upon peripheral nerve terminals, reaching full development only through substitution. Tropine is not mydriatic, while its action on the heart is influenced by esterification by means of aromatic acids; this latter effect diminishes and that on the nerve terminals is developed, according to the nature of the acid radicle introduced. The tropeines⁴ of benzoic, cinnamic and salicylic acids possess varying anæsthetic action with but little or no mydriasis. If the esterifying aromatic acid contains an aliphatic hydroxyl in the side chain containing the $-\text{O}-\text{CO}$ group, the characteristic mydriatic effect is developed as seen in mandelyl tropine (homatropine)

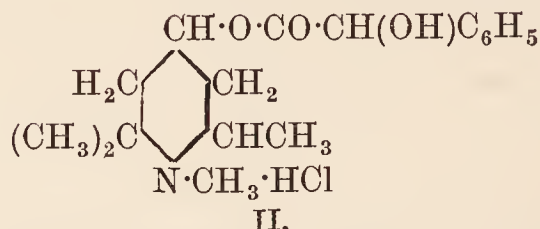


For a general account of the relation between structure and action in tropeines, see a lecture by Pyman, J. Chem. Soc. 1917, 111, 1108. It has also been found that tropeines containing either no benzene nucleus or no aliphatic group will yield mydriatic compounds.⁵ For example, α -hydroxy- β -2-pyridyl-propionyl-tropeine; o -hydroxy-benzoyl-tropeine (salicyl-tropeine); m -hydroxy-benzoyl-tropeine. By addition of alkyl halides, atropine becomes a salt of a quarternary base, which possesses a more evanescent mydriatic and lesser toxic action, such as atropine methonitrate (*eumydrin*). Of interest in this same series is the use of the unsymmetrical cyclic bases of the acetone alkamine series, for example, in the labile forms of the unsymmetrical N-alkylated bases of the triacetone-alkamines, the hydrogen of the hydroxyl, when replaced by the benzoic, mandelic, tropic or phenyl-acetic acid radicles, yields mydriatic substances. If a mandelic acid radicle is introduced in methyl-vinyl-diacetone-alkamine (I.), the mydriatic *euphthalmine* (II.) results. It is a hydrochloride

of N-methyl-vinyl-diacetone-alkamine mandelic ester, and therefore eucaine 'B' with the benzoyl group replaced by the mandelyl and the nitrogen methylated. Methyl-vinyl-diacetonamine contains two asymmetric carbons, hence forms two stereo-isomerides, an alpha form which fuses at 137° – 138° , while the beta variety fuses at 160° – 161° , the mandelic ester of the beta derivative only possesses mydriatic properties.⁶



I.



II.

The chief undesirable action of atropine in eye practice is its persistent and prolonged dilatation of the pupil. To produce a derivative of the atropine type possessing a quicker and more transitory action on the eye has been the aim of chemists. These have been attained to a greater or lesser degree in the following derivatives.

Of simpler constitution and belonging to the pyrazolone derivatives is the mydriatic mydrol.

Eumydrin. Atropine methonitrate



m.p. 163° (D. R. P. 137662, 138443), Bayer.

In action, eumydrine is intermediate between atropine and homatropine, less toxic than the former. It is especially useful in night sweats and whooping cough.

Euphthalmine. 1:2:6:6-tetramethyl-4-mandeloxy-piperidine-hydrochloride, cf. above

(U.S. Pat. 663754), Schering.

Euphthalmine is a prompt mydriatic, its effect disappears quickly. Recommended for ophthalmoscopic examinations.

Mydrol. Iodomethyl-phenyl-pyrazolone, m.p. 178° , Merck.

Mydriasin. Tropic acid ester of homotropine, obtained by reduction of anhydro-ecgonine (von Braun and Müller, Ber. 1918, 51, 235; D. R. P. 299806).

THERAPEUTIC DYES.

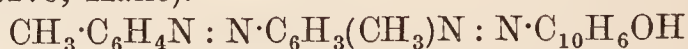
A few dyes are employed to stimulate granulation of wounds, e.g. amino-azotoluene.

Azovernin, m.p. 185° (Agfa), is amino-azotoluene rendered non-toxic by acetylation of its amino group.

Pellidol is the colourless diacetyl derivative, which strongly stimulates formation of epithelium



Biebrich Scarlet R is a compound of diazotised amino-azotoluene and β -naphthol (D. R. P. 262476, Kalle).



and is used for the same purpose.

The chief use of dyes has, however, been as

⁶ Ber. 29, 2730.

¹ Ann. Pharm. 239, 294; Ber. 21, 3065.

² Ann. Pharm. 240, 498.

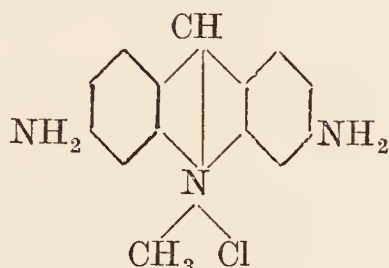
³ Jour. of Physiol. 30, 176.

⁴ Ber. 13, 106, 1080, 1137, 1549; 15, 1025; 22, 2590.

⁵ J. Chem. Soc. 1909, 1090.

antiseptics. *Malachite green*, and its ethyl analogue, *brilliant green*, are powerful bactericides. *Methylene blue* stains the malaria parasite, and was at one time recommended by Ehrlich instead of quinine. *Trypan red* (see next section) owes its name to its action on trypanosomes.

Of late acridine derivatives have come into prominence. *Phosphin* or 3-amino-9-*p*-aminophenylacridine is much more poisonous to the malaria parasite than quinine, but, nevertheless, lacks the specific curative action of the alkaloid; 3:6-diamino-acridine was first prepared by Benda (Ber. 1912, 45, 1787; D. R. P. 230412, Cassella), who also made, at Ehrlich's suggestion, the corresponding methochloride (D. R. P. 243085)



The latter substance was found to have a very powerful trypanocidal action, so that it received the name *trypaflavin*. Its bactericidal action seems to have been neglected in Germany until Browning called attention to it in England during the war (*e.g.* Brit. Med. J. 1917, 73, 76).

The tertiary base 3:6-diamino-acridine, which was also found to be strongly disinfectant, was termed in England *proflavine*, and the quaternary 3:6-diamino-10-methylacridinium chloride *acriflavine*. Both were extensively used during the war as disinfectants for surface wounds, and seem to be also of considerable value in gonorrhœa.

Other acridine derivatives have been examined, *e.g.* by Browning and Gulbransen (Proc. Roy. Soc. 1918, B, 90, 136), by Browning, Cohen, Gaunt and Gulbransen (*ibid.* 1922, B, 93, 329), and by Morgenroth, Schnitzer and Rosenberg (Deutsch. med. Wochenschr., 1921, 47, 1317). Morgenroth introduced 2-ethoxy-6-9-diamino-acridine, which is manufactured under the name of *rivanol* (Hoechst).

The hydrochloride forms a bright yellow crystalline powder, soluble 1:260 in water, giving a neutral, fluorescent solution. It is claimed to be an active antiseptic, and to retain its activity in the presence of serum. It is used in the form of a freshly prepared solution 1 or 0.5 in 1000, with the addition of at least 5:1000 of NaCl. Used for infected wounds. It may also be employed in intramuscular injections (M. Sommelet, Bull. Sci. Pharm. 1924, 30, 620; Pharm. J. 1924, 113, 45).

Attempts have been made to increase the action of dyes by forming complex salts with heavy metals, *e.g.* the silver double salt of trypaflavine (*argoflavine*), silver methylene blue (*argochrom*).

For the antiseptic action of dyes in general, see Fairbrother and Renshaw (J. Soc. Chem. Ind. 1922, 41, 134); for the pharmacology of acridine compounds, Lenz (Zeitsch. ges. exp. med. 1921, 12, 195), and also E. Laqueur, 'Die neueren chemotherapeutischen Präparate aus der Chininreihe und aus der Akridinreihe' in Ergebnisse der inneren Medizin und Kinder-

heilkunde, vol. 23, also published separately by Springer, Berlin, 1923.

ORGANIC ARSENICALS AND CHEMOTHERAPEUTIC AGENTS (PARASITOTROPICS).¹

Whilst many microbial infectious diseases are amenable to serum treatment, there are a number, especially those of protozoal origin, which can only be treated by means of chemical specifics. These react with such micro-organisms in a manner somewhat analogous to that of sera. Study in this direction has been greatly stimulated by the discovery of the protozoal parasites (trypanosoma) of the African sleeping sickness. Through the investigations of Ehrlich and others, considerable attention has been directed to the chemo-therapeutics of spirochetal diseases (syphilis, intermittent fever), and those of a malignant parasitic origin, namely the protozoal parasites of the trypanosoma, of which there are several varieties. Parasito-chemicals tend to destroy parasites in the living organism without injury to the tissues or organs, contrary to the organotropic. Ehrlich claims that all parasitotropic bodies are also poisonous to the living organism (organotropic), hence such as are curative must contain organo- and parasitotropic properties in proper proportions. Such coal-tar colours as are of value in trypanosomiasis may be divided into (a) certain azo-dyes, (b) certain basic triphenylmethane dyes as *p*-fuchsine, methyl violet, pyronine, &c. To these may be added the organic arsenicals. Ehrlich found that methylene blue was more strongly 'organotropic' than 'parasitotropic,' a dilution of 1 in six million caused cessation of movement *in vitro* when tested on the spirilla of relapsing fever, but with animal experiments it required 500 times as much of the dye. He then tried trypan red (the benzopurpurine dye formed from one molecule of tetrazotised benzidine sulphonic acid and two molecules of 2-amino-naphthalene 3:6-disulphonic acid), which was found to possess curative effects in trypanosoma of a certain type (*mal de caderas*); frequently, however, the disease reappeared after intervals. This same effect was peculiar to the azo-colours of the benzidine type. After testing a large number of colours, Ehrlich established the fact that effective bodies must be the tetrazo-colours derived from naphthalene disulphonic acids with the sulphonic groups in positions 3 and 6. They must be naphthalene derivatives containing at least one amino and two sulphonic groups. Among the diamines, the di-chloro products were the best, especially, those in which the benzene groups are connected by a divalent group (=NH,=CO). The symmetrical colours were found to be less injurious to animals. Malachite and brilliant greens with their di- and tri-hydroxy-derivatives as well as *o*-hydroxyhexamethyl-rosaniline exerted curative effects. According to Ehrlich, the toxicity of malachite green is due to its four methyl groups and that of brilliant green to its four ethyl, which is

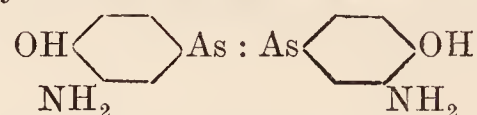
¹ G. W. Raiziss and J. L. Gavron, Organic Arsenical Compounds; G. T. Morgan, Organic Compounds of Arsenic and Antimony, Longmans, 1918; P. Ehrlich, Über den jetzigen Stand der Chemotherapie; Ber. 1909, 42, 17-47.

overcome through the introduction of a faintly acid hydroxyl group. He therefore prepared di- and tri-hydroxy-malachite greens which, when combined with trypan red, showed excellent curative effects in nagana infection. Of all the rosaniline derivatives, pararosaniline gave the best results. Most effective was the simultaneous treatment with atoxyl and trypan red or blue or fuchsine.

In conjunction with his study of the colours in treating trypanosoma infection, Ehrlich took up the organic arsenicals in combating spirochetal diseases, more especially syphilis. Inorganic arsenic destroys protozoa but cannot be given in sufficient quantities to reach the protozoa in fatal doses. The organic arsenicals are less toxic to the human organism and more so to protozoan parasites. Since the organic arsenicals are more readily eliminated, their structure should be such as to render them slowly soluble, securing thereby a slow protracted action. The aim in the study of the organic derivatives of arsenic acid has been to find products free from cumulative and secondary effects and adapted for hypodermic and intravenous use, avoiding thereby any derangement of the digestive tract.¹ The maximum typical physiologic action of arsenic is obtained from compounds containing a trivalent As, such compounds as contain a pentavalent As, which are comparatively non-toxic in the body, must first undergo reduction in the organism to the trivalent form before a physiologic action manifests itself. If this reduction takes place too rapidly, ordinary arsenical poisoning takes place. The relative rate at which this reduction takes place, producing desirable or undesirable effects, depends on the chemic structure and solubility of the organic (pentavalent) arsenic compound. It is desirable that compounds should remain in the circulatory system in contact with the parasites for a longer period of time than the inorganic arsenicals, and that the liberation of trivalent arsenic should proceed very slowly. Some of these organic arsenicals are etiotropic, having a greater affinity for the disease protozoa than the tissues of the living organism (organotropic). Inorganic arsenicals are slowly eliminated, remaining stored in the system and produce, if caution is not exercised, cumulative effects.

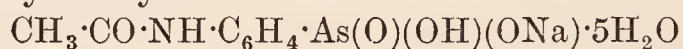
As already cited, certain triphenylmethane and azo-dyes destroy parasites in blood serum *in vitro*, atoxyl and its derivatives do not, although in the human organism (*in vivo*) they do, producing a trypanocidal action in high dilutions. This difference is most likely due to the production, by metabolic changes, in the human organism of new compounds which are active trypanocides. Experiments have shown that atoxyl is converted from a pentad to a triad organic arsenical which exerts the destructive action on spirochetes, trypanosomes, &c. According to Ehrlich, only trivalent organic arsenic compounds are of value in this respect, showing a special action on spirochetes with comparative low toxicity for the organism. For example, *p*-aminophenyl-arsenious oxide ($\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{AsO}$) and *p*-diamino-arsenobenzene

($\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{As} : \text{As} \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2$), reduction products of atoxyl, are more toxic towards trypanosomes than the corresponding pentavalent arsenic compounds. In addition, *p*-hydroxy-phenyl-arsenious oxide ($\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{AsO}$) in a dilution of one in ten million, destroys trypanosomes in one hour, while atoxyl and the hydroxy-compound, $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{AsO}(\text{OH}) \cdot (\text{ONa})$, fail in 2 p.c. solutions. The compounds of trivalent arsenic that are more extensively employed are of the type $\text{R}-\text{As}=\text{As}-\text{R}$, which show a low degree of toxicity. The most successful are dihydroxy-diamino-arseno-benzene

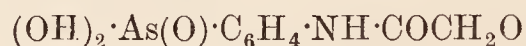


and its derivatives. Because of their excessive stability, such aliphatic compounds² as cacodylic acid [$(\text{CH}_3)_2\text{As}(\text{O}) \cdot (\text{OH})$] and arrhenal, monomethyl arsonic acid ($\text{CH}_3 \cdot \text{AsO}(\text{OH})_2$), have not found any extensive application in the treatment of protozoan infections (as syphilis, trypanosomes, spirillosis), having been superseded by the aromatic derivatives.

The earliest known of the aromatic arsenicals was atoxyl, arsanilic acid or *p*-amino-phenyl-arsonic acid [$\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{As}(\text{O})(\text{OH})_2$], which is chiefly employed in form of its sodium salt, commercially termed *soamin*, *arsamin*, or *atoxyl*. These are used in all diseases due to protozoan infection, which, however, because of their dangerous secondary effects (as blindness), must be used with caution. Less toxic is acetyl-atoxyl

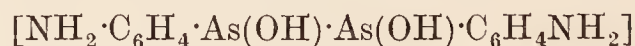


known as *arsacetin*. The corresponding *o*-toluidin acetyl compound is known as *orsudan*. Important among this class are the N-alkyl-arsonic acids, for example, phenyl-glycine-*p*-arsonic acid ($(\text{OH})_2\text{As}(\text{O}) \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{COOH}$), or similar derivatives

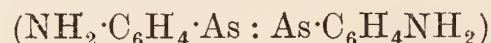


(or $\text{O} \cdot \text{CH}_2\text{CONH}$), arsenic being in a trivalent state.³

As already noted, the therapeutically active triad arsenic organics are all obtained by the reduction of their corresponding pentad compounds; thus arsanilic acid⁴ yields *p*-amino-phenyl-arsenious oxide ($\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{AsO}$), or diamino-dihydroxy-arsenobenzene



or *p*-diamino-arseno-benzene



or *p*-amino-phenyl-arsine ($\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{AsH}_2$), according to the extent of the reduction.

Arsenophenol, $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{As} : \text{As} \cdot \text{C}_6\text{H}_4 \cdot \text{OH}$, the product of the reduction of *p*-hydroxy-

² Martindale, Int. Congress of Ap. Chem. London, 1909, viii. B, 28.

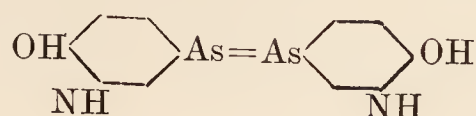
³ Aromatic arsonic acids containing an alpha-amino-acyl-arylamide group, or alpha-amino-acylamide group, or amino-acylurca group, or arsenoaryl compounds containing in each aromatic nucleus an alpha-aminoacylarylamide group (Rockefeller Institute, J. Amer. Chem. Soc. Abst. Vol. 13, No. 6, p. 634; Eng. Pats. 120383, 120384, 120385, 120381, 120382, 122819, 120385). Arsonium compounds of choline type or ethanol-tri-alkylarsonium hydroxides (D. R. P. 305772).

⁴ Eng. Pat. 17619; D. R. PP. 206057, 206456.

¹ Organic Arsenic Compounds, W. Martindale, 10, New Cavendish St., London. Also Chemistry of Synthetic Drugs, Percy May.

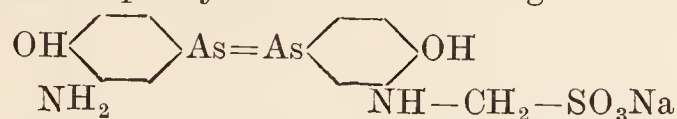
phenyl-arsonic acid, and arseno-phenyl-glycine ($\text{HOOC}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{As}:\text{As}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CH}_2\cdot\text{COOH}$)

reduced from phenylglycine arsonic acid, were found to be useful in syphilis and free from secondary effects. Thus, following his experiments with atoxyl, Ehrlich finally attained his aim in the preparation of a 4:4'-dihydroxy-3:3'-diaminoarseno-benzene



the dihydrochloride of which was introduced under the name of *salvarsan*¹ or '606.' Ehrlich found that among all the arsenical compounds tested, salvarsan showed the greatest relative etiotropic efficiency and lowest toxicity. The syphilitic infected organs retained the arsenic, while in others it was absent, which indicated a specific effect on spirochetes or their products.

Aqueous solutions of salvarsan, which is marketed in the form of a hydrochloride, do not keep, hence it must be neutralised immediately before use by means of a solution of caustic soda. The alkalinity of salvarsan should correspond to that of the blood, and its low toxicity, relatively considered in comparison with other arsenicals, is due to its insolubility in the blood. The toxicity of technical preparations is somewhat variable and should be controlled by animal experiments. It is partly due to an admixture of sulphino-acids resulting from the use of hyposulphite in the reduction of nitro-hydroxyphenyl-arsinic acid (King, J. Chem. Soc. 1921, 119, 1107). Owing to frequent occurrence of thrombosis arising from faulty neutralisation of salvarsan, a soluble derivative has been prepared by precipitating a salt of 3:3'-diamino-4:4'-dihydroxyarsenobenzene with sodium methanalsulphoxylate and dissolving the precipitate with a solution of sodium carbonate. This compound was introduced under the title of *Neosalvarsan*,² and is also known as *neoarsphenamine*, *novarsenobenzol*, *neokharsivan*, or *neodiarsenol*. This preparation is a mixture of sodium 3:3'-diamino-4:4'-dihydroxy-1-arseno-benzene-sulphoxylate with inert inorganic salts



The arsenic content of 3 parts of neoarsphenamine is approximately equal to that of 2 parts of salvarsan.

Another derivative of this class is galyl,³ a tetra-oxy-phospho-diamino-diarseno-benzene, which is used in form of its sodium salt. Many other derivatives of phenylarsinic acid, arseno-benzene and unsymmetrical derivatives of the type $\text{R}-\text{As}=\text{As}-\text{R}'$, have been found to possess therapeutic value.⁴

Recently additive metallic compounds of salvarsan have appeared; these are compounds of one mol. of cupric chloride or silver bromide with antimonyl oxide and one of salvarsan,

¹ Sold under the following names: arsphenamine, kharsivan (England); arsenobenzol (France), diarsenol (Canada); arsamino (Japan).

² D. R. P. 245756; U. S. Pat. reissue 13848.

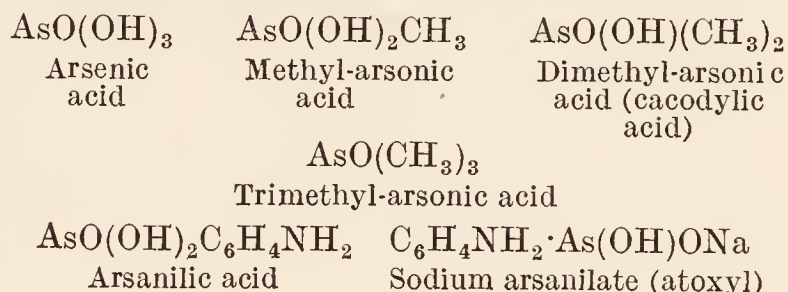
³ Eng. Pats. 3087, 9234.

⁴ Ber. 1915, 48, 509; D. R. PP. 286854-5, 251104, 270254, 251751, 251511, 254187, 269699, 269743-4-5, 271271.

prepared by precipitating a solution of the latter with a salt of the metal followed by a solution of caustic soda.⁵

In the search for spirochæte and trypanosoma remedies, attempts have been made to replace the toxic $-\text{As}=\text{O}$ group by the less toxic $-\text{Sb}=\text{O}$, with but limited success.⁶ The compounds failed either in securing a quick action on the trypanosomes before establishment of toleration or have shown an irritant action, or they failed to remain in solution at body temperature and alkalinity.⁷ Such simple compounds as *p*-amino-phenyl antimonate of sodium,⁸ potassium-ammonium antimonyl-tartrate (*Antiluetin*), and the ethyl ester of antimonyl-tartaric acid, have given fairly satisfactory results. On the other hand, sodium antimonyl tartrate has of late years been found to be a specific against Kala-azar (due to a protozoon), and against the worm *Filaria sanguinis hominis*. The injection of colloidal antimony has given excellent satisfaction in treatment of trypanosomiasis.⁹ Triphenylstibine sulphide (sulphoform) has been reported as giving good results.

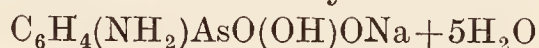
The relationship of the simpler derivatives of arsenic acid will be noted from the formulæ:



ATOXYL CLASS.

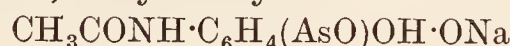
Sodium Arsanilate. Atoxyl. The sodium salt of arsanilic acid $\text{C}_6\text{H}_4(\text{NH}_2)\cdot(\text{AsO}\cdot\text{OH})_2$, 1:4 or sodium salt of *p*-amino-phenyl-arsonic acid.

Soamin. Sodium arsanilate containing five molecules of water of crystallisation



Burroughs.

Arsacetin. Sodium *p*-acetylaminophenyl-arsonate, acetyl-atoxyl



Hoechst.

Asyphil. The mercury salt of atoxyl, Charlottenburg.

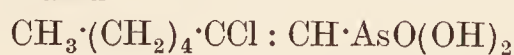
Argatoxyl. *p*-Amino-phenyl-arsonate of silver, or atoxyl with Na replaced by Ag.

Arsamon. A solution of sodium mono-methyl-arsonate, V. Heyden.

Stenosin. Di-sodium mono-methyl-arsonate.

Argentarsyl. A mixture of colloidal silver with cacodylic acid.

Solarson. Ammonium salt of chloroheptenyl-arsonic acid



Bayer.

As a simple arsenical substitute for Fowler's solution.

Elarson. The strontium salt of chloro-arsenobenzenic acid, 13 p.c. As_2O_3 , Bayer.

⁵ Ber. 1915, 48, 1634; Eng. Pats. 1247, 104496, 104497.

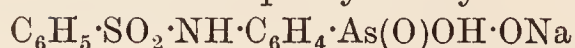
⁶ P. May, Synthetic Drugs, 215.

⁷ D. R. PP. 254421, 261825, 268451.

⁸ Proc. Roy. Soc. 1910, 249.

⁹ *Ibid.* 1909, 334; 1910, 140.

Hectine. Benzene-sulphonyl-atoxyl



(*Lancet*, June 25, 1915).

ARSENOPHENOLAMINES OR SALVARSAN CLASS.¹

Arsphenamine. Salvarsan, '606,' Kharsivan, Arsenobenzol, Diarsenol. The hydrochloride of 3-diamino-4-dihydroxy-1-arsenobenzene, corresponding to 31.57 p.c. of arsenic



(U.S. Pat. 986148; Eng. Pat. 13485), Hoechst.

Brands of Arsphenamine:

Arsaminol. (U.S. Pats. 986148, 1081897, 1081592, 1116398), Takamine Lab., N.Y.

Arsenobenzol. Same patents, Dermatologic Lab., Phila.

Diarsenol. (Canad. Pat. 133636), Synthetic Drug Co., Toronto.

Salvarsan. Same patents, H. A. Metz & Co., N.Y.

Salvarsan sodium is the soluble disodium salt.

Neoarsphenamine. Neosalvarsan, Neoarsphenamine, Novarsenobenzol, Neodiarsenol, Neokharsivan. A mixture of sodium 3-diamino-4-dihydroxy-1-arsenobenzene-formaldehyde-sulphoxylate with inert salts



The arsenic content of 3 parts of neoarsphenamine is approximately equal to that of 2 parts of arsphenamine (D. R. P. 245756; U.S. Pat. 13848), Hoechst.

Brands of Neoarsphenamine:

Neodiarsenol. (Canad. Pat. 144874, Neosalvarsan; U.S. Pat. 13848).

Silver salvarsan (Binz, Bauer and Hallstein, Ber. 1920, 53B, 416).

Galyl. Tetra-oxy-diphospho-diamino-diarsenobenzene (Eng. Pats. 3087, 9234, 1915).

Ludyl. Phenyl-disulphamino-tetra-dioxy-diamino-benzene.

Luargol. A compound of salvarsan with silver bromide and antimonyl group SbO.

'205 BAYER' AND SLEEPING SICKNESS.

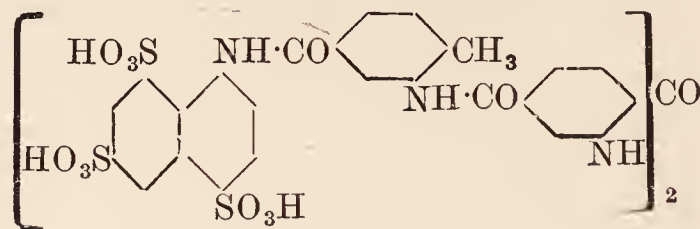
Towards the end of 1920 an advance in chemotherapy became known, which promises to provide a cure for sleeping sickness and to rival the discovery of salvarsan, at least in scientific interest. A synthetic trypanocide of great activity was reported (Haendel and Joetten, Berl. klin. Wochenschr. 1920, 57, ii. 821; see also Wenyon, Brit. Med. J. 1921, ii. 746), which is referred to as '205 Bayer.' The constitution of the substance has not been published (on account of the treatment of German patents by former enemy countries). For mice, infected with the trypanosomes of various diseases (Nagana, dourine, human sleeping sickness) the ratio of lethal dose: curative dose is extremely favourable, and cases of sleeping sickness in man appear to have been cured.

Some indication of the nature, although not the identity, of this substance, may be gathered from Bayer patents of 1914-1916: D. R. P.

¹ Chemistry, Pharmacy and Therapeutics of Salvarsan, Martindale and Westcott, London.

278122, Eng. Pat. 9472 of 1914; D. R. PP. 289163, 289270-289272; Eng. Pat. 8591 of 1916; D. R. PP. 284938, 288272, 288273, 289107, 291351. These refer to polypeptide-like carbamides of the naphthalene series, which are stated to be strongly trypanocidal.

E. Fourneau *et alii* (Compt. rend. 1924, 178, 675) state that the sodium salt of the following symmetrical urea of *m*-aminobenzoyl-*m*-amino-*p*-methylbenzoyl-1-naphthylamino-4:6:8-trisulphonic acid is pharmacologically, and may be chemically, identical with '205 Bayer.'



SYNTHETIC CATHARTICS.

The close relationship existing between the phenols and the quinones (oxidation-products of phenols) is marked in their physiological properties, more especially in their stimulating to irritant action in the intestinal canal. This is also true of the naphthaquinones and anthraquinones. The hydroxyanthraquinones stimulate intestinal peristaltic action increasing in intensity with the number of hydroxyls present; thus trihydroxyanthraquinone (anthrapurpurin)



produces severe colic through its action on the smooth muscular fibres. Best known in this respect are a number of α -hydroxy derivatives of methyl-anthraquinone, present in the glucosidal form in such cathartic drugs as aloes, rhubarb, senna, cascara sagrada, frangula, &c. (*v. RHUBARB-ROOT*). The synthetic polyhydroxy-anthraquinones are more drastic cathartics than the natural emodin of rhubarb. This suggested closing of part of the hydroxyl hydrogens by acyl or alkyl radicles, which would serve to secure a slower decomposition in the intestinal canal. It seems that the length of time the substance remains in the intestines determines the relative purgative action. Absorption causes failure to act, hence the superiority of the glucosides and less soluble acetyl derivatives.² Too rapid absorption increases undesirable action on the kidneys. The closing of all hydroxyls in this manner gave inert products. Chrysophanic acid, dihydroxy-methyl-anthraquinone, which is present in a number of the purgative drugs as the glucoside *chrysophan*, is one of the milder purgatives. Emodin, a trihydroxy-methyl-anthraquinone, is more active than chrysophanic acid. Emodin with rhamnose is the product of the decomposition of the pentoside *frangulin* from the *Rhamnus frangula*. The most active of this group is *anthrapurpurin*, 1-2-7-trihydroxy-anthraquinone.

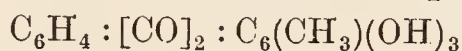
The first experiments in this direction were purgatol, a diacetylanthrapurpurin, and exodin, a mixture of the feebly active diacetyl tetramethyl ether of rufigallic acid (hexahydroxyanthraquinone) with the acetyl pentamethyl ether. The cathartic action of phenol groups containing carbonyls, as noted

² Dixon, Manual of Pharmacology.

among the anthraquinones, explains this action attributed to phenolphthalein, which, however, was discovered through accident. It may be added that phenolphthalein is to-day the most successful synthetic cathartic, because it is practically entirely eliminated unchanged from the system. Tasteless aloins, which are insoluble, decompose in the intestines producing full action. Among these are a compound of formaldehyde and aloin (D. R. P. 86449), tribromaloin, triacetylaloin, and a product of the action of a persulphate on aloin (D. R. P. 134987).

Exodin.¹ A mixture of 30 p.c. rufigallic hexamethyl ether, 23 p.c. diacetyl rufigallic tetramethyl ether, and 47 p.c. of acetyl rufigallic pentamethyl ether, m.p. 180°–190° (D. R. P. 151724), Schering.

Emodin. Trihydroxymethylanthraquinone



Istizin. 1-8-Dioxyanthraquinone, Bayer.

Purgatol (*purgatin*). Diacetyl ester of anthrapurpurin, stated to be a kidney irritant, Knoll.

Peristaltin. A glucoside from *Cascara sagrada*. May be used as intra-muscular injection, Ciba.

Phenolphthalein. Sold under such titles as purgen, purgolade, purglets, laxan, laxol, &c. Griping which sometimes accompanies phenolphthalein has been overcome by its acetyl-valeryl derivative, namely, *Aperitol*.

Sennatin. Active principles of senna for subcutaneous use, Helfenbourg.

Sennax. Glucoside of senna, Knoll.

Valerophen. Menthyl ester of phenolphthalein.

ORGANOTHERAPY.

The administration of animal glandular organs was introduced, principally by Brown-Séquard, in the middle of the last century, and has chiefly been successful in the case of certain so-called endocrine glands producing internal secretions or 'hormones.' In the case of the thyroid the whole gland can be given by the mouth, and is a specific in myxœdema and cretinism. Other glands have to be administered as extracts, by injection (*e.g.* pituitary and pancreas). The active principle of the suprarenal gland is prepared in a pure state from natural sources, and also synthetically. See the articles on ADRENALINE, PITUITARY and THYROID GLAND. The most recent achievement of organotherapy is *insulin*, the hormone of the islets of Langerhans in the pancreas, which is specific for diabetes. Its preparation is difficult, since it is destroyed by the proteolytic ferments of the pancreas; for the same reason it must be administered hypodermically. See p. 489. The pure hormone has not yet been isolated. See Annual Reports of Chem. Soc. for 1922, pp. 193–198.

For the amines tyramine and histamine derived from amino-acids by putrefaction, which are also manufactured synthetically, *v.* ERGOT. V.C.

SYRGOL. Trade name for a form of colloidal silver.

T

TAAMYA. An Egyptian food prepared by grinding the beans of a plant (family *Papilionaceae*), mixing the flour with water, spices, &c., and frying the dough, cut into small pieces, in hot cotton-seed or sesame oil. Contains moisture 22 to 33; proteins 14.2 to 16.2; fat 20.0 to 31.6; ash 3.4 to 7.1; cellulose and starch 18.0 to 29.3 p.c. (Azadian, Ann. Falsific, 1922, 15, 278; Analyst, 1922, 478).

TABBYITE. A mineral hydrocarbon, occurring in Utah and elsewhere, used as a rubber filler, and in the composition of roofing materials, &c.

TACAMAHAC. *Tacamahacin* *v.* OLEO-RESINS.

TACHHYDRITE $\text{CaCl}_2 \cdot 2\text{MgCl}_2 \cdot 12\text{H}_2\text{O}$. A mineral occurring in the salt deposits of Stassfurt in roundish, yellow, deliquescent masses.

Tachhydrite occurs in abundance in the upper carnallite region in the south-eastern portion of the Mansfeld Basin. It forms an intimate intermixture with carnallite, sylvite, and halite. It is of secondary origin, and has resulted by the action of magnesium chloride solutions on anhydrite. Synthetical experiments show that crystals of tachhydrite can take into solid solution small quantities of ferrous chlorides, but none of ferric chloride. This explains the yellow colour of the natural mineral, the ferrous chloride being then partly oxidised to hæmatite (Kling, Chem. Soc. Abstr. 1915, ii. 640).

TACHIOL *v.* SYNTHETIC DRUGS.

TAGUA NUT. The stony seeds of several species of the South American genus of palms, *Phytelaphas*, are known as tagua nuts and are

worked as 'vegetable ivory.' The two species mainly affording the commercial product are *P. macrocarpa* (Ruiz. et Pav.) and *P. microcarpa* (Ruiz. et Pav.).

TAIFUSHI OIL is the *oleum gyrovcardiæ* (*oleum chaulmoogræ*) of the Japanese pharmacopœia, and according to Keimatsu (J. Pharm. Soc. Japan, 1920, 283), is obtained from the seeds of *Hydnocarpus anthelmintica*, Pierre. It contains palmitin, but its chief constituents are glyceryl chaulmoograte, and hydrocarpate; m.p.; 22°–23°; D^{15}_D 0.952; $[\alpha]_D +51.2^\circ$; acid number 12.06; sapon. number 20.30; iodine number 85.05.

TAIGU WOOD. A wood from Paraguay, resembling guaiacum wood in appearance. Has a greenish-brown colour when fresh; becomes covered on exposure to the air with a greenish-yellow crystalline powder; and exhibits under the microscope yellow oblique prisms, together with shining, colourless, thin six-sided tables. The latter are not altered by alkalis; the former, which consist of *taiguic acid*, are reddened thereby. Strong boiling alcohol extracts from it 13.7 p.c. of a mixture of taiguic acid with resinous and waxy substances. Taiguic acid $(\text{C}_4\text{H}_4\text{O})_n$ crystallises in oblique prisms of a bright-yellow colour; is tasteless and odourless; m.p. 135°, and sublimes at 180°. Very slightly soluble in water, except under pressure; readily soluble in acetone, ether, benzene, or strong alcohol. Forms crystallisable salts with bases; those with the alkalis are deep red and easily soluble in water, the lead salt is yellow, and the silver

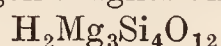
¹ Zernik. Apoth. Zeit. 19, 598.

salt cinnabar-coloured (Arnaudon, J. 1858, 264).

TAKADIASTASE. According to Y. Takahashi (Biochem. Zeitsch. 1924, 144, 199), takadiastase contains an inulase capable of hydrolysing inulin to lævulose (J. Soc. Chem. Ind. 1924, 43, B. 227).

TA-KONG. A lead glass containing ferric oxide, used by the Chinese as a red enamel on porcelain.

TALC (Ger. *Talk*). A mineral species consisting of hydrogen magnesium silicate



occurring as foliated or compact masses. The name, said to be from the Arabic 'talq,' has no doubt long been applied to various foliated minerals, such as mica and gypsum; and even at the present time it is sometimes used as a popular name for mica. The term *steatite* (Ger. *Speckstein*) is restricted to the compact, massive varieties of talc. *Soapstone* and *potstone* are impure forms of steatite; but, like the name agalmatolite (*q.v.*), they are more general in their application, and no doubt include minerals of other kinds.

Talc never occurs as distinct crystals, but only as folia or scales, which possess a perfect micaceous cleavage and a pearly to silvery lustre on their surface. The folia are flexible but not elastic, thus differing from mica. Talc is extremely soft and can be readily scratched with the finger nail; it is chosen as No. 1 in Mohs's scale of hardness. The massive varieties are often rather harder, and may range up to $2\frac{1}{2}$ –4 on the scale; but they are usually sufficiently soft to be readily cut with a knife and carved. A very characteristic feature of the mineral is its greasy or soapy feel. The colour of foliated talc is silvery-white or often a delicate shade of green; steatite is creamy-white, greyish, or greenish; and potstone and soapstone are of darker shades of colour. Sp.gr. 2·6–2·8. The mineral is very resistant to heat (no water being lost below a red-heat), to acids, and to solutions of alkalis.

Analyses: I, Green, foliated talc from Tyrol (Scheerer, 1851). II, Fibrous talc ('agalite') from Edwards, St. Lawrence Co., New York (E. S. Sperry in Dana's System of Mineralogy, 1892). III, Pseudomorphous steatite from Göpfersgrün, Wunsiedel, Bavaria (Scherrer, 1851). IV, Steatite from Hewitt mine, Swain Co., North Carolina (J. H. Pratt, Economic Paper No. 3, North Carolina Geol. Survey, 1900). V, Soapstone from Grafton, Vermont (G. P. Merrill, The Non-metallic Minerals, 2nd ed., New York, 1910). VI, Soapstone from Frankestown, New Hampshire (G. P. Merrill, *l.c.*).

	I. ¹	II.	III.	IV. ²	V.	VI. ³
SiO ₂	62·12	60·59	62·35	61·35	51·20	42·43
Al ₂ O ₃	—	0·13	trace	4·42	5·22	6·08
FeO	1·58	0·21	1·34	1·68	8·45	13·07
MnO	—	1·16	—	—	0·32	trace
CaO	—	—	—	0·82	1·17	3·27
MgO	31·15	34·72	31·32	26·03	26·79	25·71
H ₂ O	4·73	3·77	4·78	5·10	6·90	8·45
Total	99·82	100·58	99·79	100·02	100·05	99·49
Sp.gr.	2·69	2·908	—	—	—	—

¹ Also NiO, 0·24.

² Also Na₂O, 0·62.

³ Also Na₂O, 0·16; K₂O, 0·32.

Talc is of wide distribution, occurring more especially in schistose rocks and those of metamorphic origin (*e.g.* talc-schist). It is a common alteration-product of many minerals, and in the impure, massive form is intermingled with other secondary and residual products (chlorite, mica, &c.). Distinctly shaped pseudomorphs after various crystallised minerals are not uncommon.

Workable deposits, forming veins, beds, and lenticular masses, are found at many localities. Veins of steatite in the serpentine of the Lizard district in Cornwall were formerly worked for supplying material used in the manufacture of old Worcester porcelain. At Göpfersgrün near Wunsiedel in the Fichtelgebirge, Bavaria, important deposits of steatite occur at the junction of granite and limestone; the latter and its contained minerals having been largely altered by magnesium-bearing solutions emanating from the granite. Deposits are also worked in the Pyrenees and in the Italian, Swiss, and Austrian Alps. The best qualities for toilet and medicinal purposes have long been obtained near Pinerolo in the Chisone valley, Piedmont. At several places in India large quantities of steatite and potstone are quarried for carving into bowls, plates, cups, and other domestic utensils and ornamental objects. The largest amounts (about 120,000 tons per annum) are obtained in the United States. The fibrous talc ('agalite,' *q.v.*), which occurs as an alteration-product of tremolite and enstatite in crystalline limestones, in the Gouverneur district, St. Lawrence Co., New York, is employed in large quantities in the manufacture of writing and printing papers. Steatite and soapstone are obtained from Virginia, North Carolina, Vermont, &c. In the Verdite mine, near Barberton, Transvaal, vertical bands of steatite, 15 ft. in thickness, occur in ultra-basic rocks.

The uses of talc are many. Powdered talc enters largely into the composition of toilet-powders; it is used as a dry lubricant; for dressing leather, cloth, rubber, &c.; for foundry facings; for adulterating soap and other goods; in the manufacture of paper and paints (enamel paints, and especially those for preserving the iron work of bridges and ships); as a non-conducting material for covering steam-pipes; as a preservative coating on stone work. Steatite (the well-known 'French chalk') is used for marking on cloth, metal, glass, slate, and blackened paper. It forms the tips of gas-burners, backs of stoves, furnace linings, &c. Being soft and readily worked, it is a favourite material for elaborate carvings, especially in the East. It has also been used as a source of magnesium salts, particularly the sulphate. Sawn slabs of soapstone are extensively used in America for benches (in chemical laboratories, hospitals, &c.), acid tanks, sinks, laundry tubs, hearth-stones, foot-warmers, and even for building purposes. Being a good insulator, it is used for electrical switchboards, and the floors of generating stations.

Another mineral also applied to many of these purposes is pyrophyllite (H₂Al₂Si₄O₁₂) (*q.v.*; *v.* also AGALMATOLITE).

References.—Talc (1913–1919), Imp. Min. Res. Bur. London, 1921. Talc and Soapstone in Canada, H. S. Spence, Canada, Mines Branch, 1922, No. 583. On American talc and soapstone

v. G. P. Merrill, *The Non-metallic Minerals*, 2nd ed., New York, 1910. R. H. Vail, *Mineral Industry*, vol. 19, New York, 1911. J. S. Diller, *Mineral Resources of the United States* (U.S. Geol. Survey), ii. 1911. J. H. Pratt, *Talc and Pyrophyllite Deposits in North Carolina*, Economic Paper, No. 3, N. C. Geol. Survey, 1900. On Indian steatite, v. G. Watt, *Dictionary of the Economic Products of India*, 6, 1893. L. J. S.

TALIPOT. A variety of starch obtained from a palm, *Corypha umbraculifera* (Linn.). Known in Ceylon as 'raw palmira root flour.'

TALLOW. In commerce a distinction is made between *beef* tallow and *mutton* tallow. The former is obtained from oxen, cows, and calves; the latter from sheep and goats. The distinction is, broadly speaking, supported by chemical differences in the composition of the respective glycerides, mutton tallow being as a rule richer in stearin than beef tallow.

The quality—especially the hardness—of tallow depends on the breed and the age of the animal, and to some extent on the food. The fat from the male beast is generally harder than that obtained from the female. Animals fed on grass yield a harder fat than those fed with oilcakes; brewery refuse produces especially soft tallow. Hence we have all gradations from the hard South American beef tallow to home-melt tallow of somewhat softish consistence.

The 'rough fat' is delivered with the adhering tissue, &c., to the tallow-melters, and is rendered at a temperature of about 100° (*see Rendering under OILS, FIXED, AND FATS*).

The fats from different parts of the carcase, although of unequal value, are not kept separate, unless the fat be intended for the manufacture of oleomargarine or of tallow of best commercial quality.

At present the tendency is to collect the rough fat, as far as possible, in large rendering establishments fitted up with modern appliances. Hence the slaughter-houses in large towns—especially on the Continent of Europe—have at present as an adjunct a tallow-rendering establishment. These are found on the greatest scale in the large packing-houses of the United States of America as also of South America.

For the production of tallow for the manufacture of margarine the more valuable kidney fat ('suet,' 'edible fat') and bowel fat ('midgerum fat') is dealt with separately and not mixed with the caul- (or kell-, *i.e.* *omentum*) fat and the fat from other parts of the carcase.

By melting this selected fat at low temperatures—not exceeding 50°—the 'premier jus' is obtained (*see MARGARINE*).

The following commercial brands of tallow are differentiated:—

(1) Rendered tallow, which contains all the fat from the carcase.

(2) 'Premier jus.'

(3) Pressed tallow (tallow stearine, beef stearine, mutton stearine, oleostearine).

(4) Oleomargarine, oleo oil.

The first-named quality of tallow, *viz.* 'rendered tallow,' is frequently expressed in hydraulic presses for the preparation of 'tallow stearine' and 'tallow oil.'

It is almost impossible to estimate the quantity of home-melted tallow produced in European countries, as the production is

scattered over the smallest establishments, embracing even those of butchers in villages.

None of the European countries has for some years past been exporting tallow, the quantities exported from the United Kingdom being in fact re-exports. Russia, which up to about the beginning of this century was a tallow-exporting country, has been forced to draw upon the world's supply for her own demands. Even the United States of North America, which for many years have been large suppliers of tallow, have practically ceased to export tallow, they themselves importing tallow from South America.

The chief sources of tallow—in addition to the 'home-melt' productions—are at present Australasia, South America, and to a smaller extent New Zealand. Large quantities of tallow are expected in the near future from Rhodesia.

The imported tallows are chiefly of the quality enumerated above under No. 1, *viz.* rendered tallow containing all the fat from the carcase. These tallows are sold according to their titer (titre), solidifying point of fatty acids and colour (*see OILS, FIXED, AND FATS*).

As regards colour the commercial brands are differentiated as 'good colour,' 'off colour,' 'no colour,' &c., and are merely judged by the standards agreed upon between sellers and buyers on the London market. There is a further distinction made between 'beef,' 'mutton,' and 'mixed' tallows.

During recent years, in consequence of the great demand for edible fats, the production of 'premier jus' for export to Europe has been established on a large scale in oversea countries. Such tallow is not only carefully prepared from selected rough fat, but it is also filtered over fuller's earth, so that it arrives in a perfectly sound state in Europe. When carefully packed, it will keep for months in good condition. Thus the production of oleomargarine and oleostearine for export to Europe has assumed considerable dimensions during the last few years.

On pressing tallow for the production of 'stearine,' *tallow oil* is obtained as a by-product; this is liquid or semi-solid according to the temperature at which it has been expressed. Tallow oil is chiefly used in admixture with mineral oils as a lubricating oil. Its solidifying and melting-points, as also its iodine values, naturally vary according to the conditions under which the tallow has been expressed.

Beef tallow.—(For characteristics *see OILS, FIXED, AND FATS*.) Beef tallow when freshly rendered is nearly white, free from disagreeable odour, and almost tasteless. Such quality is represented by 'home-melt beef tallow.' Imported tallow passes through all gradations, from 'bleached' white to slightly yellowish tallow (Australian), through darker yellow (North American, South American) to, finally, the 'off-coloured' lowest grades (North American, Australian 'no colour').

Tallow was until recently considered to consist exclusively of the glycerides of palmitic, stearic, and oleic acids. The amount of olein used to be calculated from the iodine value. It is not unlikely that owing to the influence of vegetable oils given with the food (oilcakes, &c.) less saturated acids than oleic acid may be found.

Bömer has shown that by frequently repeated crystallisation of beef tallow from ether,

approximately $1\frac{1}{2}$ p.c. of pure tristearin can be isolated, whilst a palmitodistearin is also present.

On the assumption that the fatty acids of tallow consist of palmitic, stearic, and oleic acids only, the composition of a sample may be arrived at by determining the proportion of stearic acid (*see* OILS, FIXED, AND FATS). The proportion of oleic acid can be calculated from the iodine value; the difference gives then the amount of palmitic acid.

Beef stearine is the hard portion of tallow left in hydraulic presses after removal of the tallow oil (*see* above). Beef stearine obtained from 'premier jus' is used for edible purposes in the manufacture of margarine, as also in the manufacture of compound lards and in the preparation of 'suet substitutes.'

The amount of free fatty acids in tallow varies considerably with the state of purity. In freshly rendered tallows, the proportion is negligible and rarely exceeds 0.5 p.c.; in commercial samples, the percentage of free fatty acids may rise to 25 p.c. and even more.

For the complete commercial examination of tallow, *see* Lewkowitsch, Chem. Tech.

Mutton tallow.—(For characteristics, *see* OILS, FIXED, AND FATS). Mutton tallow closely resembles beef tallow; it is frequently mixed with the latter and is then sold as 'mixed tallow.' Mutton tallow is, as a rule, harder than beef tallow, and consequently its solidifying and melting points, as also those of its fatty acids, are higher. It is more liable to turn rancid than beef tallow. For this reason it cannot be used in the manufacture of first-class butter-substitutes or high-class toilet soap.

Bömer has shown that by frequently repeated crystallisation of mutton tallow from ether approximately 3 p.c. of pure tristearin and 4–5 p.c. each of steardipalmitin and palmitodistearin can be isolated. J. L.

TALMI GOLD. An alloy of 86.4 p.c. copper, 12.2 p.c. zinc, 1.1 p.c. tin, and 0.3 p.c. iron, used in the manufacture of trinkets.

TA-LOU. A Chinese term for a glass flux used for enamelling on porcelain. Consists mainly of a lead silicate containing a small quantity of copper (Ebelmen and Salvétat, Ann. Chim. [iii.] 35, 344).

TAMARINDS. The fruit of *Tamarindus indica* (Linn.) freed from the outer part of the pericarp and preserved with sugar. Tamarind pulp contains about 12–14 p.c. of tartaric acid, partly free and partly as potassium bitartrate, and might be used as a source of tartaric acid, as the acid can easily be recovered by the methods used in the production of the acid from wine-lees after heating the pulp to 160° in an autoclave (Sudborough and Vridhachalam, J. Indian. Inst. Sci. 1920, 3, 61).

Tamarinds from the Kistna district of Madras, when extracted with boiling water, showed a tartaric acid content of 9.55 p.c. By fermenting and washing the broken material in a filter-press the yield was increased to 12.5 p.c., and 11.5–12.5 p.c. of alcohol could be distilled off. Autoclaving at 60–70 lbs. pressure is essential for the satisfactory treatment of tamarinds for tartaric acid. Filtration is improved if the residual acid liquor after distilling off the alcohol is autoclaved together with the extracted tamarind residue. For every 1000 lbs.

of tamarinds 15–19 gals. of 96 p.c. alcohol should be recoverable, together with 14 lbs. of crude potassium hydrogen tartrate and 190 lbs. of calcium tartrate (F. Marsden, J. Ind. Inst. Sci. 1923, 5, 157; J. Soc. Chem. Ind. May 4th, 1923, P. 375 A).

TAMBAC or **TOMBAC.** *White copper.* An alloy of 85 p.c. copper and 15 p.c. zinc.

TAMBOR TREE (*Omphalea oleifera*). A common tree in various parts of western Salvador, known by the vernacular names of *tambor*, *palo de queso*, *hoja de queso*, and *palo de Jabón* ('soap tree'). The name *tambor* ('drum') relates to the fact that the perpendicular taproot is dug out by the natives and in drying shrinks at each end, and becomes hollow in the middle, thus forming a resonant object which is employed as a kind of drum. Valued for its supposed medicinal virtues. The seeds of the tambor yield a syrup which is said to have pectoral properties and to be efficacious in the cure of persistent coughs. The oil of the seeds likewise is employed for affections of the chest, and a decoction of the bark, drunk after meals, is said to be effective as a flesh-forming substance. When the trunk is wounded, a milky latex issues from it, coagulating into an amber-coloured mass, which soon turns black. This is employed for dyeing, and is said also to be a good remedy for diarrhoea and dysentery. The immature fruits are boiled and eaten as a vegetable. The most valuable product is the oil, in which the seeds are very rich—about 33 p.c. It is yellowish white, has a sweet flavour, and is odourless. It is used in cookery like olive oil and in perfumery and in the manufacture of soap (Standley, Pharm. J. 1923, 479).

TANACETONE *v.* KETONES.

For the effect of heating tanacetone (*thujone*) with ammonium hydrogen sulphide, *see* Agostinelli (Chem. Soc. Abstr. 1914, i. 1133); alkylation, *see* Haller (*ibid.* i. 66); the conversion of tenacetone into thujamenthone, Godchot (*ibid.* i. 973).

TANARGAN. A combination of tannin and silver albuminate.

TANGHIN or **TANGUIN.** The celebrated judicial poison used by the inhabitants of Madagascar has been examined by Arnaud. It was known that the toxic principle was contained in the almonds of the *Cerbera Tanghin* (Hook.) belonging to the family of the *Apocynaceæ*. The almonds contain about 75 p.c. of fatty matter which could not be got rid of by simple pressing. By treating with carbon disulphide, however, which does not take up the tanghinin, the fat was extracted. Subsequent boiling with strong alcohol, and evaporation, yield a crystalline substance of powerful toxic properties. It has a strong action upon the heart, resembling strophanthin and ouabaine (J. Soc. Chem. Ind. 1889, 211; 1888, 765), having, however, a more general convulsive action than these bodies.

Tanghinin forms colourless, rhombic, anhydrous crystals which melt at 182° , and are very sparingly soluble in water, but easily in strong alcohol. It is lævo-rotatory, and has the following composition: Carbon, 65.74; hydrogen, 8.19; oxygen, 26.07 (Arnaud, Compt. rend. 1889, 108, 1255; *ibid.* 109, 701). Cf. DIGITALIS.

The poisonous properties of a tanghin or ksopo extracted from the plant *Menabea vene-*

bata (Baill.) of the family *Asclepiadaceæ* and used by the Sakalaves, are described by Camus (Compt. rend. 1903, 136, 176).

TANNALBIN. Albumin tannate. Used as an intestinal disinfectant.

TANNASE. A diastase found in nut-galls, sumac leaves, &c., capable of hydrolysing tannin (Fernbach, Compt. rend. 131, 1214; Poltevin, *ibid.* 131, 1215).

According to Knudson (J. Biol. Chem. 1913, 14, 185) there is a progressive increase of tannase in *Aspergillus* and *Penicillium* with increased concentration of tannic acid in Czapek's solution containing 10 p.c. sugar. In a full nutrient solution containing 2 p.c. tannic acid as a source of carbon the addition of sucrose decreases the secretion of tannase. *Aspergillus* secretes more tannase (or more active tannase) per unit weight than *Penicillium*. The production of the enzyme is stimulated in both moulds by gallic and especially by tannic acids. See also Freudenberg and Vollbrecht (Chem. Soc. Abstr. 1922, i. 285). For the estimation of tannase, see Rhind and Smith (*ibid.* 1922, ii. 407).

TANNASPIDIC ACID *v.* FILIX MAS.

TANNIC ACID *v.* TANNINS.

TANNIDES. In a considerable number of cases alkaloids and tannides occur together in the same cells. It is not, however, always necessary to assume the existence of alkaloid-tannide compounds. Such compounds may be present where the presence of alkaloids is not shown by the usual tests. Many alkaloids and tannides are products of excretion, and insoluble alkaloid-tannide compounds may also be regarded as such. They may, however, have some physiological function (Rosenthaler and Mosemann, Schweiz. Apoth. Ztg. 1924, 62, 13, from Chem. Zentr. 1924, i. 1678; Chem. Soc. Abstr. 1924, 126, O. 924).

TANNIGEN (*Acetannin*). Used in the treatment of diarrhoea, $C_{14}H_8(COCH_3)_2O_9$ (Corfield and Short, Pharm. J. 1924, 113, 115).

TANNING *v.* LEATHER.

TANNINPHENOLMETHANE. Trade name for a combination product of tannin, formaldehyde, and phenol.

TANNINS (*Acides tanniques*, Fr.; *Gerbstoffe*, Ger.). This term has been applied to a large class of substances which have been found in many plants and are distinguished by the following characters: they have an astringent taste; give a blue-black or green coloration with ferric salts; are precipitated by a solution of gelatin, by albumen and by alkaloids; unite with hide to form leather.

It was formerly believed that only one tannin existed, and it was assumed that the difference in properties of tannin from different sources was due to the presence of foreign matter. It is, however, now well known that tannin from different sources frequently varies both in composition and in properties, and although it is probable, owing to the difficulty of obtaining these compounds in an even approximately pure condition, that the number of distinct individuals may not be so great as is usually supposed, there can be no doubt that at least three important classes of tannins exist in nature. The earliest suggestion was to divide the tannins into two classes—the iron-blueing tannins and the iron-greening tannins—according to their behaviour

towards salts of iron, and it was considered that whereas the former were pyrogallol compounds, the latter were derived from catechol. This differentiation appears in the main to be correct, and the employment of ferric chloride for this purpose, or better, iron alum as a preliminary step, is of general application; but on the other hand, it is to be borne in mind that the presence of acid, alkali, or organic impurity has considerable effect upon the colour production. Thus, although the method is no doubt of service in many cases even with the plant infusion, its exact significance can only be ascertained from the coloration given by the purified tannin itself.

Mitchell (Analyst, 1923, 48, 2) has based a method of estimating pyrogallol tannins and their derivatives on the violet coloration given by substances containing a pyrogallic group with a ferrous tartrate reagent. Osmium tetroxide in neutral or slightly alkaline solution gives a violet coloration with both pyrogallol and catechol tannins and their derivatives, and the reaction, which is capable of detecting 1 part of gallic acid in 3 millions, can be used for the colorimetric estimation of these tannins, a solution of pure pyrogallol, catechol, or gallic acid being used as the standard for the comparison (Mitchell, Analyst, 1924, 49, 162).

Stenhouse (Proc. Roy. Soc. 11, 405) believed that those tannins which give blue-black precipitates with ferric salts are mostly glucosides. Wagner (Zeitsch. anal. Chem.) made a distinction between *pathological* and *physiological* tannins, and considered that the former class represented by gallotannic acid only existed in pathological formations of certain species of oak and sumach (*Rhus javanica*, Linn., and *R. semilata*, Murr.), whilst the latter class include all tannins which are produced under normal conditions of plant life. As, however, gallotannic acid has been found to exist in some plants as a physiological tannin, Wagner's classification is untenable.

Böttger (Ber. 1884, 17, 1123) has examined the action of bromine on aqueous tannin extracts, and determined the percentage of bromine contained in the precipitated bromo products. As a result, it was shown that certain tannins may be grouped together according to the amount of bromine which they take up.

Mangrove tannin . . .	42.15
Hemlock bark tannin . . .	43.6
Quebracho tannin . . .	44.5
Mimosa tannin . . .	49.36
Chestnut oak tannin . . .	50.48
Terra japonica tannin . . .	53.2
Spruce bark tannin . . .	52.8

A large amount of attention has been given to the classification or identification of aqueous extracts of tanning materials, by the coloured and other effects given by certain reagents. It remains to be decided whether in all cases these reactions in reality arise from the tannin itself.

The more important methods which may be used to classify the tannins into groups according to our present knowledge of these substances are as follows:—

Coloration with ferric chloride or iron alum (see above).

Digestion with boiling dilute sulphuric acid.—In this method of procedure, three definite

reactions may be observed: (a) the hydrolysis of the tannin with formation of gallic acid (gallotannic acid); (b) the precipitation of ellagic acid (ellagitannic acid); (c) the gradual production of an amorphous red-coloured precipitate known as a 'phlobaphene' (catechol or phlobatannin).

Precipitation with bromine water indicates the presence of a so-called catechol or phlobatannin (Procter, *Leather Industries Handbook*, 1898).

Pine wood and hydrochloric acid test.—If a deal shaving be moistened with a solution of phloroglucinol and then with strong hydrochloric acid, a deep red-violet colour due to the formation of phloroglucinol vanillein is produced. Resorcinol reacts similarly giving a blue-violet (Procter). These colorations are an indication of the presence of a phloroglucinol or resorcinol nucleus in the tannins. Gallotannin and ellagitannin solutions do not react in this manner.

Diazobenzene chloride.—Solutions of certain tannins in the presence of alkali or alkaline acetates give a red-coloured precipitate of the azobenzene tannin with this reagent, a fact which indicates with some certainty the presence of a phloroglucinol or resorcinol grouping. Gallotannin and ellagitannin do not react in this manner.

Fusion with alkali.—Procter (*Leather Industries Handbook*, 1898) recommends adding 20 grms. of tannin to 150 c.c. of a solution of potassium hydroxide of sp.gr. 1.20 and concentrating the liquid during three hours until it becomes pasty. Or 5 to 10 parts of caustic potash and a few drops of water are heated with one part of the tannin to 210°–240° for twenty minutes. Gallotannin, by this method, gives gallic acid, and possibly traces of pyrogallol, whereas the so-called catechol tannins yield protocatechuic acid or other allied acid, alone, or together with phloroglucinol or resorcinol, &c.

Heating with glycerol.—The tannin (1 gm.) is heated with 5 c.c. of glycerol slowly raising the temperature from 160°, and keeping it for half an hour between 200°–210°. The product diluted with 20 c.c. of water is extracted with ether, the extract evaporated and the residue tested for pyrogallol or catechol. According to Trimble (*The Tannins*), paraffin wax may be employed in place of glycerol.

Formaldehyde test.—When an aqueous solution of a so-called catechol tannin is treated with formaldehyde and a little hydrochloric acid and gently warmed the tannin is completely precipitated. Pyrogallol tannins do not yield an entirely insoluble compound in this manner. This reaction, discovered by Stiasny (*Der Gerber*, 1905, 185), has by numerous writers been assigned to Jean and Frabot (*Ann. Chim. anal.* 1907, 12, 49).

Lead acetate test.—(Stiasny and Wilkinson, *Collegium*, 1911, 475 (2 ix.), 318.) All natural tannins are completely precipitated by lead acetate solution in so far as the filtrate from the precipitate does not give the iron test. In the case of catechol or phlobatannins this precipitate is dissolved by dilute acetic acid, whereas with the gallotannins the lead compound is insoluble or but partially soluble. The test is preferably made by adding 10 c.c. of acetic acid (10 p.c.) to 5 c.c. of the tannin solution, and then adding 5 c.c. of lead acetate (10 p.c.). No precipitate is

thus produced in the case of the catechol or phlobatannins.

By these methods it is easy to divide the tannins into three classes, usually distinguished as (1) gallotannins, (2) ellagitannins, and (3) catecholtannins. Since the discovery of synthetic tannins by Fischer and Freudenberg (*Annalen*, 1911, 384, 225), it is evident that this nomenclature, as applied to the first group, is imperfect. Thus, whereas the term 'gallotannin' is in reality only applicable to compounds containing pyrogallol nuclei and in fact merely relates to digallic acid and its derivatives, it is now known that diprotocatechuic acid, diresorcylic acid, and digentisic acid, members of the same group, possess tanning property. On this account it is considered more reasonable to distinguish such tannins by the term 'depside,' a nomenclature which is due to Fischer and Freudenberg, although it is not suggested that such a group is absent in the other tannins.

Again, as regards the so-called 'ellagitannin' group (2), new tannins belonging to this class may also be either synthesised or isolated in the future. The term 'ellagitannin' is therefore here replaced by 'diphenyldimethylolid,' the name by which the group mother substance is known.

Exception is again to be taken to the designation 'catechol' tannin (3) for reasons similar to those given above and which are discussed later in this article, and this name is also replaced by 'phlobatannin,' in that these compounds, apparently without exception, possess the property of yielding phlobaphenes. In respect of this latter group, it is to be noted in connection with the qualitative tests above enumerated that the formation of phlobaphene and of precipitates with bromine water and with formaldehyde sufficiently indicate the presence of this variety of tannin, because these compounds may not all react with pine wood and hydrochloric acid, or diazobenzene chloride, or give protocatechuic acid as one of their decomposition products.

There appears to be ample evidence also of the existence of special varieties of glucoside belonging to this third class, distinguished by their extremely hygroscopic nature and the fact that they are insoluble or nearly so in acetic ether. They give, however, the well-marked reactions of the phlobatannins. None of these compounds has yet been obtained in a pure condition, but when they are digested with boiling dilute mineral acids a sugar and phlobaphene appear to be mainly produced.

Methods of isolation.—All the well-known tannins are dissolved by hot water, and yield precipitates with lead acetate solution, and thus by decomposing the well-washed lead precipitate from a plant infusion in the moist condition with sulphuretted hydrogen a crude solution of the tannin is obtained. This can be concentrated *in vacuô* over caustic potash or sulphuric acid. In the place of lead acetate, stannous chloride was employed by Proust in 1798 (*Ann. Chim.* 25, 225), who is credited with being the first to prepare tannic acid in a nearly pure condition. As, however, the tannin usually exists in the plant side by side with yellow colouring matter, either in the free state or as glucoside, and other secondary substances

soluble in water, a fractional precipitation with lead acetate is preferably adopted, in which case the middle portion usually yields the purest tannin (Grabowski, Sitz. Ber. 1867, 55, ii. 567; Trimble, *The Tannins*, 1892, i. 85). A preliminary treatment with lead acetate in the presence of a little acetic acid is serviceable in some cases for the precipitation of coloured impurities. Probably the solvent most extensively employed since 1880 in the investigation of tannins has been ethyl acetate, in which case it has been usual to agitate a solution of the substance or extract of the plant with this solvent. A preliminary addition of salt or sodium sulphate to the liquid is beneficial.

Certain tannin glucosides, owing to their sparing solubility in ethyl acetate, cannot be satisfactorily isolated in this manner, and the method is not applicable to the case of mineral salts of the tannin, in which the preliminary production and subsequent decomposition of the lead salt is to be recommended. Numerous methods have been adopted for the purification of the tannin thus prepared, and are given under the head of the special substance for which they have been employed.

In many cases it has been found preferable to extract the tannin matter with an organic solvent rather than with water. This is, as a rule, to be advised, as the crude substance is thus more readily isolated in a concentrated form. Indeed, one of the oldest methods of separating tannins from other substances is that of Pelouze (*Ann. Chim.* 1834, 55, 337), who exhausted powdered gall-nuts with commercial ether. Various mixtures of alcohol, ether, and water have been recommended, and also dilute alcohol in the case of gall-nuts for preparing gallotannic acid, although these methods must not be considered of special advantage for the isolation of tannins as a whole. Probably the most efficient solvent for general purposes of investigation is acetone which was employed by Trimble for the percolation of numerous tannin matters (*The Tannins*).

In tanning the tannins are fixed by the animal fibre. A reliable tannin test must therefore demonstrate this specific property, and such a test has been described by E. Atkinson and E. O. Hazelton, and developed and extended by Phyllis H. Price (*Analyst*, 1924, 49, 25; *Bio-Chem. J.* 1922, 16, 516), the method consisting in fixing the tannin on gold-beater's skin and subsequently staining the skin with ferric chloride. Non-tannins are not fixed on the gold-beater's skin, which consequently is not stained by this reagent. It is thus possible to detect 0.00005 grm. of gallo-tannin in 1 c.c. of solution with the use of either ferrous sulphate, ferrous chloride, or amyl nitrite fumes in place of ferric chloride. On addition of dilute hydrochloric acid skins previously treated with pyrogallol tannins are completely decolorised, whereas those treated with catechol tannins have a reddish stain left on them. *See also* Jordan and Ware (*Pharm. J.* 1924, 113, 102; *Analyst*, 1924, 49, 442). This fact may be used as a test for phlobaphenes (*Analyst*, 1924, 49, 28).

Atkinson and Hazelton's test (*Chem. Soc. Abstr.* 1922, ii. 7, 93) is modified as follows: The gold-beater's skin may be successively soaked in 2 p.c. hydrochloric acid solution instead of

water, washed thoroughly to eliminate the acid, treated for 30 minutes with 1 c.c. of the solution to be tested, washed for 15 minutes, treated with 1 c.c. of 1 p.c. ferrous sulphate or chloride solution for 15 minutes, and washed for 2 minutes. Staining of the skin indicates the presence of tannin. If the liquid is to be tested for phlobaphenes, the gold-beater's skin, treated as above, is then left covered with 1 c.c. of 5 p.c. hydrochloric acid solution for 2 minutes and afterwards washed for 2 minutes (P. H. Price, *Analyst*, 1924, 49, 25; *Chem. Soc. Abstr.* 1924, 126, ii. 209).

For a new classificatory test for drugs containing tannins, *see* Ware (*Pharm. J.* 1924, 113, 104; *Analyst* 1924, 49, 442).

R. J. Browne (*J. Soc. Leather Trades Chem.* 1923, 9, 365) has suggested an alternative method of analysis of tannin solutions which rests on quite a different principle to the usual hide-powder method, and appears to overcome one of the recognised weaknesses of the older method, viz. that part of the gallic acid in a tan liquor is returned as tannin. The method depends on the fact that tannins are colloids, and by filtration through a suitable membrane can be separated from non-tans, which are crystalloids. The membrane described is prepared by soaking filter-paper in a 6 p.c. solution of collodion in alcohol-ether, allowing it to dry till quite opaque (not longer), and then keeping it under water for an hour or until required. Thus prepared, the membrane is of standard permeability. For use it is placed in a modified form of Bechhold's pressure-filtration apparatus, and the tannin solution containing 4 grms. of tan per litre is filtered through it. The method gives a figure for tannins and insolubles. Comparative results obtained by this method and the hide-powder method show agreement in the case of various fresh tanning materials. In the case of solutions containing gallic acid (*e.g.* spent tan-liquors) the results do not agree, since gallic acid passes through the membrane, but is largely retained by hide-powder (*Analyst*, 48, 1923, 569).

For a method of measuring the brown colour of solutions of tannin extracts, *see* H. R. Proctor (*J. Soc. Chem. Ind.* 1923, 42, 73).

A reagent for the colorimetric determination of small quantities of tannin is prepared by boiling together 100 grms. of sodium tungstate, 30 grms. of arsenic pentoxide, 300 c.c. of water, and 50 c.c. of concentrated hydrochloric acid, under a reflux condenser for 2-3 hours, and then diluting to 1 litre. This reagent is unaffected by proteins, phenols, or dextrose, but is sensitive to reducing agents. The colour produced with tannic acid is permanent for one hour. The sample (20 grms.) is ground to pass a No. 40 sieve, placed in a 300 c.c. Erlenmeyer flask with 100 c.c. of petroleum ether, shaken occasionally, and allowed to stand overnight. The mixture is filtered through a dry paper and washed with 5 portions of 20 c.c. of petroleum ether. The residue is dried, returned to the flask, and extracted (cold) with 200 c.c. of 95 p.c. alcohol for 16 hours. After filtering through a dry paper, 10 c.c. of the filtrate are placed in a urine centrifuge tube, 2 c.c. of a 10 p.c. lead acetate solution are added, and the tube is placed in a water bath at 75° until the precipitate floccu-

lates. The tube is centrifuged for 3 minutes, the supernatant liquid is decanted, and the residue allowed to drain as much as possible; 5–10 drops of 5 p.c. sulphuric acid (just sufficient to dissolve the lead tannate and precipitate the lead completely) are added to the residue and thoroughly mixed. Water is added almost to fill the tube, which is again centrifuged for 3 minutes. The clear liquid is decanted into a graduated flask. In a similar flask is prepared a standard solution of gallotannic acid (containing 1–2 mgs.), which has been freed from gallic acid by extraction with ether. 2 c.c. of the reagent are added to each flask, followed by 10 c.c. of a 20 p.c. solution of sodium carbonate. The mixtures are diluted, allowed to stand for 5 minutes, and the colours compared by ordinary methods (P. Menaul, J. Agric. Res. 1923, 26, 257; J. Soc. Chem. Ind. 1924, 43, B. 226).

Experiments carried out with purified gallotannic acid and dry hide powder showed that a correction is necessary for dissolved hide substance in tannin analysis—a correction is also applied for the amount of inorganic residue obtained in a blank determination. The results showed that the amount of hide substance obtained in a blank determination was twice as much as the hide substance dissolved by the weakest tannin solution. Repeated washing of the hide powder-tannin compound causes hydrolysis, and some tannin is removed. The hydrolysis of more lightly tanned powders is greater. Ferric chloride is not a satisfactory reagent for detecting the presence of non-tannins in wash waters. The experiments were repeated with washed hide powder, and slightly higher results were obtained, but the general result was the same as with dry unwashed hide powder. All the tannin is not removed from solutions of pure tannin except at infinite concentration. There is an increase in the percentage of tannin removed with increasing concentration. It is desirable to use as concentrated a solution as possible for detannising in order to obtain the greatest degree of accuracy. The concentration specified in the official method, detannising with washed hide powder and not correcting the residue obtained after detannising, gives an apparent percentage of tannin of 98.4 p.c., or an error of 1.6 p.c. At a concentration of 2.3 grms. per 100 c.c., this error is reduced to 0.7 p.c., which would only amount to 0.2 p.c. of tannin in a 25 p.c. extract (I. G. W. Schultz, J. Amer. Leather Chem. Assoc. 1923, 18, 524–532; J. Soc. Chem. Ind. 1923, 42, 1189 A).

I. DEPSIDE GROUP.

Tannin, Tannic acid, Gallotannin, Gallotannic acid is found to the largest extent in galls which arise from the puncture of insects of the genus *Cynips* on the leaves and buds of various species of oak, more especially the *Quercus lusitanica* (Lam.), and on a species of sumach, *Rhus semilata* (Murr.). Aleppo galls, derived from the young shoot of the oak and which are the best variety of oak gall on the market, contain 50–60 p.c. of gallotannic acid, whereas Chinese galls from sumach yield as much as 70 p.c. In smaller amount it occurs also in numerous plants, and is probably the main tannin of various sumachs, of valonia, divi-divi, and algarobilla.

The methods employed for the isolation of gallotannic acid from galls are more or less modifications of that of Pelouze, which consists in extracting finely powdered galls with commercial ether. The extract separates into two layers, the upper consisting of an ethereal solution of gallic acid, wax, and resinous substances, whereas the lower represents a concentrated solution of gallotannic acid which, on evaporation, remains as a porous mass. In place of the ether a mixture of 75 p.c. commercial ether and 25 p.c. alcohol can be employed. The method of Leconnet (Annalen, 1836, 18, 179) consists in stirring powdered galls into ether until a thin cream results, pressing the mixture and repeating the operation until tannin is no longer removed. According to Domine (J. Pharm. Chim. 1844, [3] 5, 231) it is advantageous to allow the powdered galls before extraction to remain for some time in a moist atmosphere, and Pelouze's process with this modification was adopted by the British and United States pharmacopœias.

For the manufacture on the large scale, Chinese or Japanese galls are preferably employed owing to their richness in tannin. The finely powdered material is stirred with sufficient water at 50°–60° to form a concentrated aqueous extract, and after filtration the clear liquid is agitated with one-fourth of its volume of ether until an emulsion results. After standing for several days, the upper ethereal liquid which has separated is removed, and the lower layer, which contains all the tannin matter, is run into a still and the ether which is present recovered. After cooling the syrupy liquid is spread out on sheets of tin, and heated by means of a steam coil, when the gallotannic rapidly puffs up and dries.

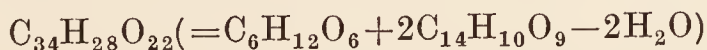
Thus prepared the commercial tannin contains some quantity of gallic acid, plant wax, glucose and other impurities; to remove these the material may be washed with ether, or the aqueous solution shaken with ether, or the aqueous liquid fractionally precipitated with common salt, the precipitate dissolved in ethyl acetate, and the tannin recovered by evaporation under reduced pressure. Trimble (The Tannins, 85) treats a 5 p.c. solution of the tannin with 10 p.c. lead acetate, drop by drop, until the precipitate, at first yellow coloured, ceases to be granular and is colourless. This is collected, the filtrate agitated two or three times with ethyl acetate and the extract evaporated. The colourless product, which still contains gallic acid, is redissolved in water, and the solution, after agitation with ether, evaporated under reduced pressure. Finally, the residue dissolved in ether by the aid of a little water is again brought rapidly to dryness under reduced pressure, and thus obtained is colourless and gives no reactions for gallic acid or glucose. With the object of preparing a homogeneous product, Walden (Ber. 1898, 30, 3154) has employed dialysis, and also the precipitation of a solution of the purest commercial tannin in ethyl acetate with benzene. Rosenheim and Schidrowitz (Chem. Soc. Trans. 1898, 73, 882) point out the extreme difficulty of removing the last traces of gallic acid from the tannin and employ a mixture of ether and acetone for this purpose. Paniker and Stiasny (Chem. Soc. Trans. 1911, 99, 1821) state, however, that the process of Rosenheim and Schidrowitz only

partially removes gallic acid. The method suggested by Perkin, which consists in neutralising a solution of the tannin with sodium bicarbonate, extracting the mixture with ethyl acetate, and subsequently precipitating the substance from the extract with benzene, gives a product free from even traces of gallic acid (see also Iljin, Ber. 1909, 42, 1731). Fischer and Freudenberg (Ber. 1912, 45, 919) find the addition of dilute sodium hydroxide to the tannin solution until faintly alkaline before extraction with ethyl acetate is similarly beneficial.

Gallotannic acid as found in commerce consists of an amorphous powder possessing a faint yellow colour, although when exhaustively purified it is colourless. It is readily soluble in water and alcohol, more sparingly in ethyl acetate, insoluble in pure ether, chloroform, or benzene. With solutions of ferric salts, gallotannic acid gives a bluish-black coloration or precipitate, according to the concentration, whereas ferrous salts give with strong solutions only a white precipitate which gradually turns blue in the air. Many metallic salts give precipitates with the tannin, those of lead and tin being colourless, whereas the copper and silver compounds possess a brown tint. Cold alkaline solutions absorb oxygen from the air and darken in colour with production of the so-called *meta-gallic acid*. When boiled hydrolysis occurs, gallic acid being formed. Gallotannic acid precipitates most alkaloids and gives precipitates with albumen and gelatin, the latter, according to Trunkel (Zeitsch. Biochem. 1910, 26, 458), in quantitative amount.

Analyses of gallotannin by Berzelius, Pelouze, Mulder, Bijlert, Strecker, Gautier, Trimble, Dekker, and Walden have been in fairly close agreement, varying from about C=51.5 to C=52.3; H=3.7 to H=4.1 p.c. Iljin (Ber. 1909, 42, 1735) has suggested higher numbers (C=54.13; H=3.22), the correctness of which he has again emphasised (J. pr. Chem. 1910, [ii.] 82, 422; cf. Nierenstein, *ibid.* 1909, 42, 3552). Mulder (J. pr. Chem. 1849, 48, 90) was the first to assign to gallotannin the formula $C_{14}H_{10}O_9$, and this was subsequently adopted by Schiff (Ber. 4, 231), and until recently generally accepted as correct. Very numerous salts of gallotannic acid have been described which are in fair agreement with this view, of which *ammonium tannate*, $NH_4C_{14}H_9O_9$, *potassium tannate*, $KC_{14}H_9O_9$, *sodium tannate*, $NaC_{14}H_9O_9$, and *barium tannate*, $Ba(C_{14}H_9O_9)_2$ (Buchner, Annalen, 53, 361) may be given as examples. For a complete list reference should be made to Beilstein (1896), ii. 1926.

Gallotannic acid isolated from plants is said to contain free glucose which is difficult to eliminate. Strecker (Annalen, 90, 340) indicated the possible existence of a glucoside of the formula $C_{27}H_{22}O_{17}$, although Schiff (*ibid.* 170), while agreeing that unaltered tannin is probably a glucoside of digallic acid, preferred the formula



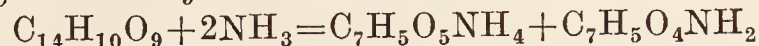
This corresponds to a yield of 23 p.c. of glucose; whereas in natural tannin about 22 p.c. is said to have been detected.

When gallotannic acid is heated at from 160°–215°, water, carbon dioxide, and *pyrogallol*

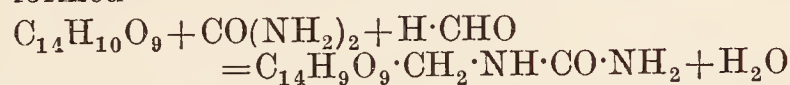
are evolved, and a dark-coloured non-volatile substance known as *metagallic acid* is produced. According to Trimble (*l.c.*) the best yields of *pyrogallol* are obtained by raising the temperature slowly to 215° and then keeping it between 190°–210° for half an hour. Digested with boiling dilute mineral acids, gallic acid is produced, and Wetherill, who employed for this purpose 50 grms. of tannic acid and 500 c.c. of sulphuric acid (1 vol. acid+4 of water), obtained a yield of 87.4 p.c. of gallic acid. Knop (Annalen, 170, 44) states he obtained 95 p.c., and Stenhouse the theoretical amount, whereas Trimble (*l.c.*) considers that when pure gallotannic acid is heated with a 2 p.c. solution of absolute hydrochloric acid, gallic acid only is produced. This reaction was formerly assumed to be expressed by the following equation:—



Boiling alkaline solutions also produce gallic acid, but hot aqueous ammonia yields *ammonium gallate* and *gallamide* as follows:—

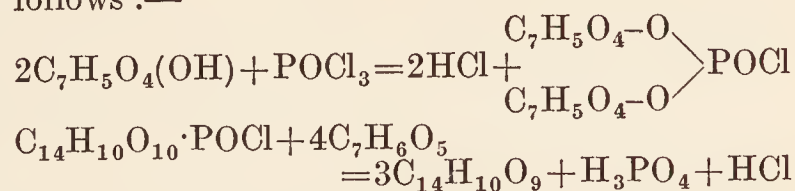


According to Voswinkel (D. R. P. 1905), on adding formaldehyde to an aqueous solution of tannin and carbamide in molecular proportion, a precipitate of *methylene tannin carbamide* is formed—

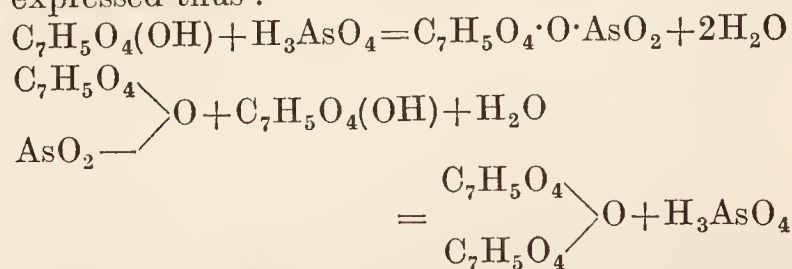


It is a yellow powder decomposing at about 220° and is insoluble in organic solvents with the exception of alcohol.

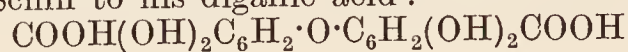
By heating barium gallate with silver nitrate, Löwe (J. pr. Chem. 1867, 102, 111) obtained a substance resembling gallotannic acid, and the same compound, together with ellagic acid, was also produced by the action of arsenic acid on gallic acid. Schiff (Ber. 1871, 4, 231) stated that when gallic acid was heated with phosphorus oxychloride at 100°, and subsequently at 120°, digallic acid was produced and this had the same percentage composition and properties as natural gallotannin. The reaction (Annalen, 1873, 170, 56) most probably occurred as follows:—



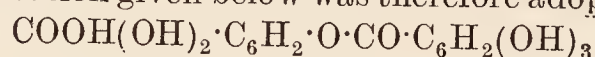
and there was indeed evidence of the intermediate formation of a phosphorus compound. Further, it was noticed that pure tannin gives some ellagic acid when heated with phosphorus oxychloride at 130°–140°. Schiff (Ber. 1871, 4, 967) also corroborated Löwe's statement that digallic acid is produced from gallic acid by means of arsenic acid. The reaction could be expressed thus:—



The following constitution was first assigned by Schiff to his digallic acid:—



and indeed by means of acetic anhydride only a tetra-acetyl compound was apparently produced. Later (*l.c.* 1873) a study of acetyltannin which was obtained as warty nodules, m.p. 137°—Trimble (*The Tannins*, i. 87) gives m.p. 139°; Nierenstein (*Collegium*, 1905, 23), 129°–131°; Dekker (*Ber.* 1906, 39, 2497), 129°; and Nierenstein (*ibid.* 1907, 40, 917), 146° (*cf.* Böttinger, *ibid.* 1884, 17, 1478)—indicated that this possessed the formula $C_{14}H_5O_9Ac_5$, and the constitution given below was therefore adopted—



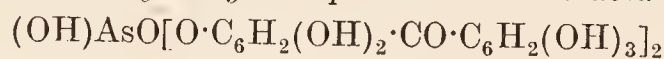
A penta-acetyl derivative was also given by digallic acid prepared both by the phosphorus oxychloride and arsenic methods (*Ber.* 1873, 68, 72), and there appeared at the time to be no doubt that this artificial product was identical with the natural tannin. Phosphorus pentachloride and phosphorus trichloride again produced digallic acid from gallic acid. According to Geschwender (*Inaugural Diss. Munich*, 1906), penta-acetyldigallic acid can be obtained in a crystalline condition from dilute alcohol.

By heating protocathechuic acid with arsenic acid, Schiff (*Ber.* 1882, 15, 2589) obtained his *diprotocatechuic acid* in the form of a hygroscopic glassy mass. This possessed the characteristics of a tannin, and with boiling dilute mineral acids was converted into protocathechuic acid.

Dipyrogallol carboxylic acid from pyrogallol carboxylic acid and *phloroglucinol tannic acid* from phloroglucinol carboxylic acid were also prepared (*Annalen*, 295, 40).

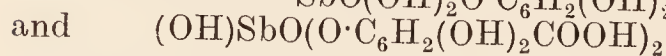
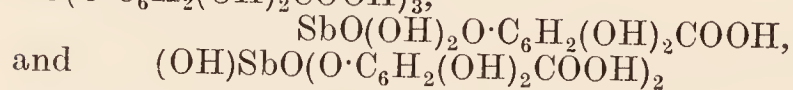
Freda (*Ber.* 11, 2033; 12, 1576), however, did not obtain digallic acid by the interaction of gallic and arsenic acids, but only an arsenic compound, which on treatment with sulphuretted hydrogen gave gallic acid.

Biginelli (*Gazz. chim. ital.* 1909, 39, ii. 68) obtained from arsenic acid and gallic acid *arsenic gallic acid* $AsO(OH)_2 \cdot O \cdot C_6H_2(OH)_2COOH$, *arsenic digallic acid* $(OH)AsO[O \cdot C_6H_2(OH)_2COOH]_2$, and *dihexahydroxybenzophenone arsenic acid*



The second of these compounds, Biginelli suggests, forms one of the constituents of Schiff's artificial tannin.

Similar compounds are produced by the action of phosphoryl chloride or antimonie acid on gallic acid (Biginelli, *ibid.* 283) to which the following formulæ have been assigned:—



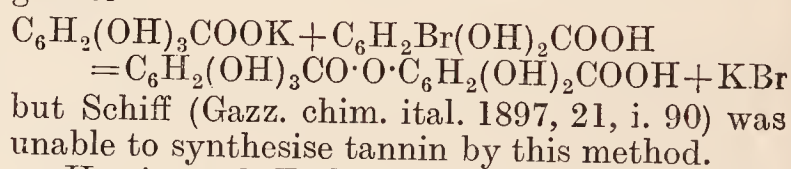
All these substances react as tannins, and it seems possible that Schiff's digallic acid preparations are in reality similarly constituted. On the other hand, Walden (*Ber.* 1898, 81, 3168) prepared Schiff's digallic acid by the arsenic acid method, and although he noted the difficulty of completely removing arsenic, this appeared to be absent from the purified compound (*cf.* also Nierenstein, *Chemie der Gerbstoffe*, Stuttgart, 1910, 44).

By heating gallotannin with benzoyl chloride, Böttinger (*Ber.* 1889, 22, 2707) prepared a *benzoyltannin* in the form of a sandy light yellow coloured powder. Sisley (*l.c.*) and Dekker (*l.c.*) describe similar products. Vournasos (*Le tannin de la noix de galle*, 27), on the other hand,

describes *pentabenzoylgallotannin* as a well-defined crystalline compound.

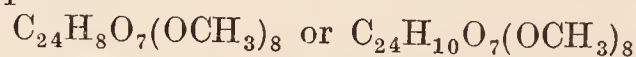
By heating a mixture of ethyl gallate and pyruvic acid with sulphuric acid, Böttinger (*Ber.* 1884, 17, 1476) prepared a substance $C_{14}H_{10}O_9 \cdot 2H_2O$, which he at first regarded as digallic acid. It consisted of a very hygroscopic mass which had the properties of a tannin, gave a penta-acetyl compound, and with lead acetate solution yielded a dull yellow precipitate. As, however, by digestion with boiling dilute hydrochloric acid no gallic acid was produced, it could only be an isomeride of natural gallotannin.

According to Hunt (*Chem. News*, 52, 49), a substance which behaves in many respects like tannin can be prepared by the interaction of monobromoprotocatechuic acid and potassium gallate—



but Schiff (*Gazz. chim. ital.* 1897, 21, i. 90) was unable to synthesise tannin by this method.

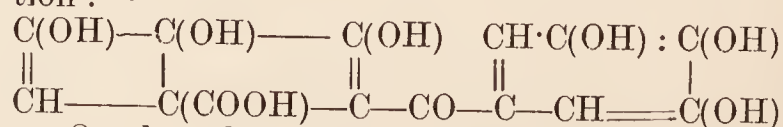
Herzig and Tscherne (*Ber.* 1905, 38, 989) obtained *methyltannin* by the action of diazomethane on gallotannin suspended in ether, and describe it as a colourless amorphous powder, melting-point 124°–126°. It had the composition—



is dextro-rotatory and when hydrolysed gives a mixture of *trimethylgallic acid* and *3:4-dimethylgallic acid*. The percentage of methoxyl found, however, approximates to that required for a pentamethylgallotannin (Herzig, *ibid.* 1908, 41, 83). Later, Herzig and Renner (*Monatsh.* 1909, 30, 543) consider that their methyltannin may possibly be a mixture of substances which have approximately the same composition, and indeed contain pentamethoxy derivatives of the tannin constituents described by Nierenstein (*sec* below). Rosenheim (*Chem. Soc. Proc.* 1905, 21, 157), by means of methyl sulphate, obtained a compound having the composition of a tannin pentamethyl ether.

Whereas, for a considerable time, Schiff's formula was generally recognised as the best-known expression for the constitution of gallotannin, it had been pointed out by Scheibler in 1866 (*Zeitsch. Zuckerind.* 16, 33) by van Tieghem in 1867 (*Ann. Sci. Nat.* [v.] 8, 210) and by Gunther in 1872 (*Ber. Pharm. Ges.* 5, 172) that natural gallotannin was optically active.

Owing no doubt to the idea that unless carefully purified, gallotannin obstinately retains traces of sugar, this fact did not attract special attention until Schiff (*Gazz. chim. ital.* 1895, 25, [ii.] 437) noted that the pure substance possesses a dextro-rotation ($[\alpha]_D = +14^\circ$ to $+67^\circ$). In order to provide for the assymetric carbon atom, a modification of his earlier formula was accordingly necessary, and he now suggested that gallotannin should be represented as a ketonic compound of the following constitution:—



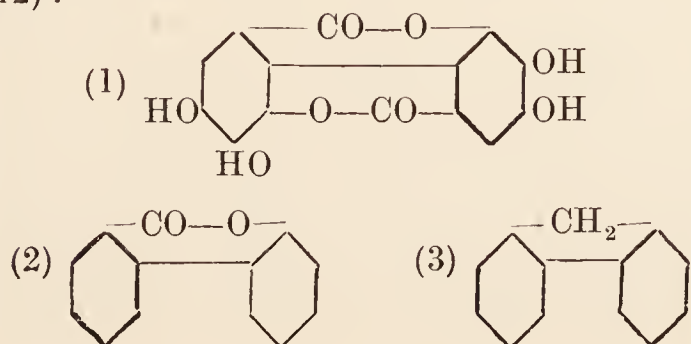
On the other hand, by the action of phenylhydrazine under varied conditions, no hydrazone could be prepared from gallotannin.

According to Walden (Ber. 1897, 30, 3151), who examined the purest samples of commercial tannin available, these products, as already indicated by Schiff, vary considerably in optical activity, having $[\alpha]_D$ from $+15^\circ$ to $+67^\circ$, and are evidently mixtures.

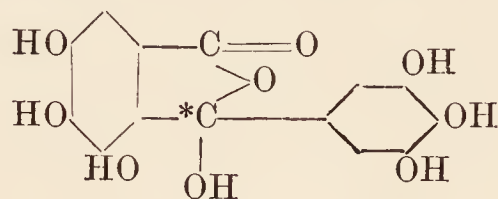
Whereas Paternò (Zeitsch. physikal. Chem. 1899, 4, 458) found the molecular weight of tannin in water to be 2643–3700, and that of Schiff's digallic acid 660, Sabanéeff (J. Russ. Phys. Chem. Soc. 1890, 22, 104) showed that in acetic acid gallotannin gave the figure 1322. Kratff, again (Ber. 1899, 32, 1613), found for gallotannin in water 1587–1626.

Walden (Ber. 1899, 31, 3167), on the other hand, showed that the molecular weight indicated by Schiff's digallic acid in boiling acetone is about 316, whilst samples of Merck's and Schuchardt's tannin in the same solvent respectively gave figures of 753–763 and 1350–1360. Moreover, the affinity coefficient of Schiff's digallic acid is $K=0.0012$, whereas that of tannin, which varies greatly with the concentration, is from $K=0.0001$ to $K=0.00006$. Spectrometric examination of solutions of gallotannin and digallic acid showed also that their absorption powers for all regions of the spectrum are entirely different, and from these facts there could be no doubt that gallotannin and Schiff's digallic acid are distinct compounds. Moreover, it was not possible to regard digallic acid as the inactive modification of gallotannin. Rosenheim and Schidrowitz (Chem. Soc. Trans. 1898, 73, 878), who examined samples of commercially 'pure' gallotannins, again pointed out the wide limits through which the rotation of these varied, the minimum being $[\alpha]_D +11^\circ$ and the maximum $+74.2^\circ$. The important point was also indicated that these commercial products could be separated into fractions the rotatory powers of which varied from $[\alpha]_D +0^\circ$ to $[\alpha]_D +75.2^\circ$, and it was further concluded that in each of the original samples a homogeneous gallotannin exists, possessing an optical activity of about $[\alpha]_D +75^\circ$. As a confirmation of this point it was noted that the quinine salts and penta-acetyl compounds prepared from gallotannins of $[\alpha]_D +11^\circ$ up to $[\alpha]_D +75^\circ$ were identical in rotatory power *inter se* with those prepared from the purified gallotannin (*cf.* also Iljin, Ber. 1914, 47, 985).

According to Nierenstein (Ber. 1905, 38, 3641) when gallotannin is distilled with zinc-dust, diphenylmethane is produced, a result which is in harmony with Schiff's formula for digallic acid, in that it has been previously found that ellagic acid (1) and diphenylmethylol (2) (Graebe, *ibid.* 1903, 36, 212) by a similar method give fluorene (3) (*cf.* also Perkin and Nierenstein, Chem. Soc. Trans. 1905, 87, 1412):—



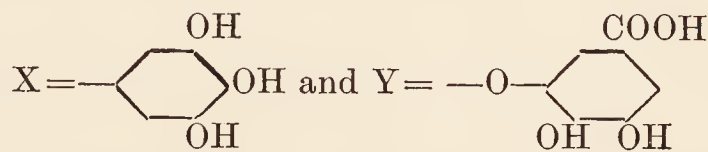
Dekker (Ber. 1906, 39, 2497; *ibid.* 3784) suggested that gallotannin should be represented as a derivative of phthalic anhydride—



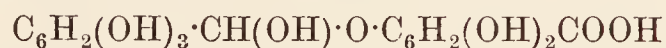
and it was considered that this formula is in harmony with the optical activity, almost complete hydrolysis to gallic acid and the formation of diphenylmethane. According to numerous workers, however, gallotannin gives only a penta-acetyl derivative, whereas such a constitution indicates seven hydroxyl groups, and though Dekker describes a hexa-acetyl tannin $[\alpha]_D +64.4^\circ$, the existence of this is doubtful.

Later, however, Dekker (De Looistoffen, 1908, ii. 30, 1908) was unable to confirm the production of diphenylmethane from tannin as observed by Nierenstein (*l.c.*), and obtained only diphenyl. Nierenstein (Chemie der Gerbstoffe, 1910, 47), however, maintains the correctness of his former work.

Lloyd (Chem. News, 1908, 97, 133) concludes that gallotannin contains three digallic groups united to each other to form a six-membered ring of the type $CXY \begin{smallmatrix} O \cdot CXY \\ O \cdot CXY \end{smallmatrix} O$ in which



Nierenstein (Ber. 1907, 40, 916) separates acetylgallotannin, which, on analysis, behaves as a penta-acetyl compound, into two amorphous components, (a) m.p. 203° – 206° , present in small quantity, and (b) the main product, m.p. 166° . The former when hydrolysed gives gallic acid, and on oxidation by means of potassium persulphate and acetic acid, ellagic acid. By means of zinc-dust the penta-acetyl-tannin, m.p. 203° (Ber. 1908, 41, 77), may be reduced to the acetyl derivative, m.p. 166° . Again, the compound, m.p. 166° , which is termed *acetyl-leucotannin*, is not a fully acetylated compound, but on further treatment gives hexa-acetyl-leucotannin, m.p. 159° . Thus gallotannin is considered to be a mixture of digallic acid and leucotannin,

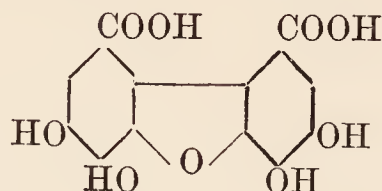


the latter being evidently the main component of the mixture.

Penta-acetyl-leucotannin (Ber. 1909, 42, 1122) is hydrolysed by boiling dilute sulphuric acid with formation of *gallic aldehyde* and *gallic acid* as its formula suggests, and when oxidised with persulphate and sulphuric acid in boiling acetic acid gives, in addition to ellagic acid, a red amorphous product, *purpuro-tannin* ($C=69.14$; $H=2.84$), which on distillation with zinc-dust yields naphthalene.

In a later paper (Nierenstein, Annalen, 1912, 386, 318) the formula $C_{14}H_8O_9$ ($C=52.5$; $H=2.5$) is assigned to this compound, and the *quinoline* salt $C_{14}H_8O_9 \cdot 2C_9H_7N$, *tetra-acetyl*

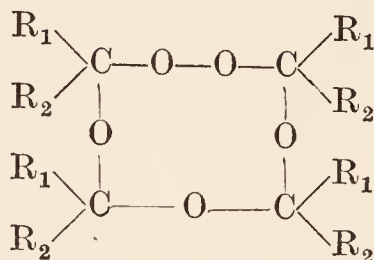
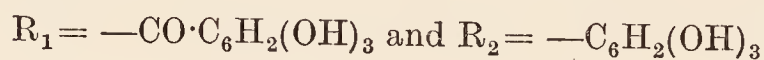
compound, m.p. 324°–327°, *tetrabenzoyl* compound, m.p. 279°–281°, and *tetramethylether*, m.p. 242°–244°, are described. By distillation with zinc-dust it gives *diphenylene* and not naphthalene, as was at first considered to be the case. With piperidine at 180° it gives 1:2:7:8 *tetrahydroxydiphenylene oxide* $C_{12}H_8O_5$, m.p. 334°–338°, with hydriodic acid and phosphorus *diphenylene oxide*, and from these results appears to possess the following constitution:—



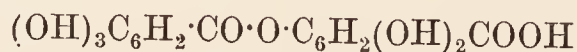
Iljin, on the other hand, who studied the action of zinc-dust on a boiling 10 p.c. aqueous solution of tannin for 15–20 hours, obtained an amorphous substance which has $[\alpha]_D^{18.4} + 24.1^\circ$ in 95 p.c. alcohol, gives coloured precipitates with metallic salts, and gallic acid without gallic aldehyde when heated with 20 p.c. sulphuric acid in a current of hydrogen (J. pr. Chem. 1909, [ii.] 5, 80, 332).

According also to Herzig and Renner (Monatsh. 1909, 30, 543), tannin methyl ether (*l.c.*) is practically unaffected by boiling with acetic acid, zinc, sodium acetate, and acetic anhydride, no leuco compound being thus produced.

Iljin (J. Russ. Phys. Chem. Soc. 1908, 39, 470; Chemie der Gerbstoffe, 1910, 49) obtained two phenylhydrazine derivatives, $C_{74}H_{58}N_6O_{30}$ and $C_{98}H_{82}N_{14}O_{26}$, from gallotannin. He suggests for gallotannin the formula $C_{56}H_{40}O_{33}$, and proposes the following constitution, in which

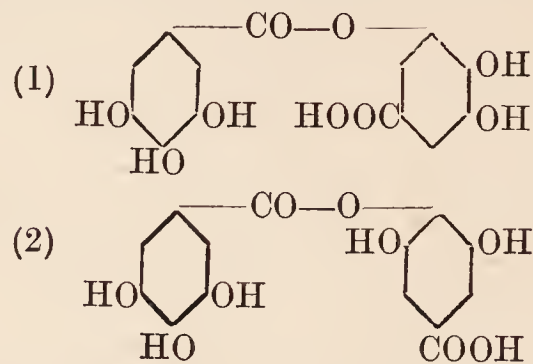


E. Fischer (Ber. 1908, 41, 2875), by coupling tricarbomethoxygallyl chloride with dicarbomethoxygallic acid, obtained a product which, on hydrolysis, gave a substance, m.p. 275°–280°, crystallising in prisms or needles. This was considered to be possibly a mixture of digallic acid with gallic acid, but was subsequently shown (1911, see below) to be a slightly impure *digallic acid*



According to Nierenstein (Ber. 1910, 43, 628), by converting gallotannin into the carboethoxy derivative, hydrolysing this with pyridine and repeating the operation three or four times, there is obtained a digallic acid $C_{14}H_{10}O_9 \cdot 2H_2O$, crystallising in small needles from alcohol and water (1:3) which sinters at 214° and melts at 268°–270°. It (1) is optically inactive, when hydrolysed gives gallic acid, and on oxidation with hydrogen peroxide ellagic acid, but is not identical with Fischer's digallic acid (2) which

does not yield ellagic acid. Nierenstein formulates these compounds as follows:—



Penta-acetyldigallic acid, needles, m.p. 211°–214°, *pentabenzoyldigallic acid*, needles, m.p. 187°–189°, *pentacarbethoxydigallic acid*, small cubes, m.p. 194°–195°, and *sodium digallate* are described.

By digestion with boiling acetic anhydride and zinc-dust, penta-acetyldigallic acid gives *dl-hexa-acetyl-leucotannin*, m.p. 154°–155°, cubes, and may be separated by means of the strychnine salt into *l-hexa-acetyl-leucotannin*, having m.p. 151° and $[\alpha]_D^{15} - 4.6^\circ$, and *d-hexa-acetyl-leucotannin*, having m.p. 153°–154° and $[\alpha]_D^{20} + 121.5^\circ$.

Iljin (J. pr. Chem. 1910, [ii.] 82, 422) re-determined the molecular weight of specially purified gallotannin in acetone, and found values of 1247–1637, confirming the results of Sabanéeff and of Walden (*l.c.*). Accordingly he considers that gallotannin must consist largely of a complex derivative of gallic acid, distinct from the digallic acid and leucotannin of Nierenstein.

When gallotannin is boiled for four hours with zinc oxide the filtrate does not react with ferric chloride. The residue decomposed with sulphuric acid gives gallic acid and the compound previously obtained by the action of zinc-dust on tannin (*l.c.*) in approximately equal amount (Iljin, *ibid.* 1910, [ii.] 81, 327). Manning (J. Amer. Chem. Soc. 1910, 32, 1312) prepares *ethyl gallotannate* $C_{51}H_{52}O_{26} \cdot 5H_2O$, yellow crystals, m.p. 157°, by passing dry hydrogen chloride into an alcoholic solution of gallotannin; this on hydrolysis gives ethyl alcohol, dextrose, and gallic acid. This compound may be synthesised by treating a mixture of ethyl gallate and dextrose with phosphoryl chloride.

Fischer and Freudenberg (Annalen, 1911, 384, 225) coupled dicarbomethoxygallic acid and tricarbomethoxygallyl chloride in alkaline solution, and by hydrolysis of the resulting product obtained a pure *digallic acid*. It crystallises in needles, is much less sparingly soluble in water than gallic acid (approximately twelve times), and melts at 275° (corr. 282°) with decomposition. With ferric chloride it gives a blue-black coloration and possesses the properties of a tannin. For a description of the diprotocatechuic acid, digentisic acid, and di- β -resorcylic acid of these authors, see below.

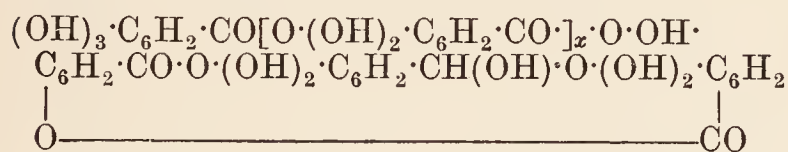
Paniker and Stiasny (Chem. Soc. Trans. 1911, 99, 1819) investigated the acid character of this substance by the diazo-acetic ester method of Fraenkel (Zeitsch. physikal. Chem. 1907, 60, 202), because, according to the previously expressed view of Böttiger (Ber. 1884, 17, 1503), Dekker (*ibid.* 1906, 39, 2497), and Walden (*ibid.* 1898, 31, 3170), no free carboxyl group is present in this compound. It is shown that gallotannin is to be regarded as an acid,

the affinity constant being of a distinctly higher order than that shown by phenols.

Gallotannin can be divided into two parts by saturating its solution with sodium bicarbonate, one part being soluble in ethyl acetate, while the other forms a sodium salt and is insoluble. Thus the former product is shown to be only half as acid as that which is set free on acidifying the sodium salt in solution. The experiments favoured the view of Kunz-Krause (Schweiz. Wochensch. Chem. Pharm. 1898, No. 38), Walden (*l.c.*), Aweng (Rev. Int. Falsif. 1898, 11, 29), and Nierenstein (*l.c.*), that gallotannin is a mixture of two or more chemical individuals.

With alcoholic potassium acetate, gallotannin gives a precipitate of the potassium salt which appears to have the unimolecular formula $C_{14}H_9O_9K$. This compound is devoid of optical activity.

According to Nierenstein (Annalen, 1912, 388, 223), when an aqueous solution of tannin is reduced with zinc-dust by Iljin's method (*l.c.*) *dl-leucodigallic acid*, fine needles, m.p. 278° – 280° , is produced, and the same compound can also be prepared by the reduction of digallic acid. By means of the carbethoxy derivative, this can be resolved into *l-leucodigallic acid*, m.p. 276° – 277° , which has $[\alpha]_D^{15} - 70.26^\circ$, and *d-leucodigallic acid*, m.p. 276° – 277° , which has $[\alpha]_D^{19} + 104.2^\circ$ in water. As leucodigallic acid does not possess tanning property, it cannot be present in gallotannin, and the author now therefore discards his theory that the latter is composed of a mixture of digallic and leucodigallic acids. Tannins are accordingly now considered to consist of *polydigalloyl-leuco-digallic-anhydrides*—



Schering's tannin, employed by this author, gave digallic and leuco-digallic acids in the proportions 3 : 1 or 4 : 1 (*cf.* Ber. 1907, 40, 916), and was consequently a digalloyl, tri- or tetra-leucodigallic anhydride. For further details the original paper must be consulted.

E. Fischer and Freudenberg (Ber. 1912, 45, 915) take an entirely different view of the constitution of gallotannin, and announce the important fact, not generally suspected, that this compound contains a *glucose* nucleus. Purified preparations of gallotannin have $[\alpha]_D^{20}$ approximately $+70^\circ$, and these samples, when hydrolysed with acid, yield gallic acid and a small amount of dextrose. Gallotannin is most probably a compound of dextrose with five molecules of digallic acid, of the nature of penta-acetyldextrose, and such a constitution will agree with its high molecular weight, optical activity, faint acidity, and ready solubility in water. Synthetical tannin compounds, derivatives of dextrose, are described, the properties of which favour this suggestion. Tricarbomethoxygalloyl chloride in chloroform solution reacts with dextrose in the presence of quinoline, to form penta-tricarbomethoxygalloyl glucose, from which, by hydrolysis with alkali, *pentagalloyl-glucose* is produced. It is a yellow

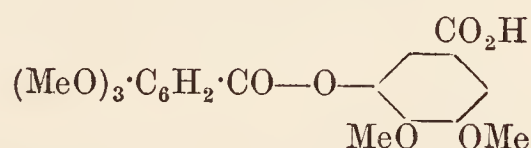
powder of astringent taste, possesses the power of precipitating gelatin solutions, and has $[\alpha]_D + 31^\circ$ to $+35^\circ$ in water, or $+44.4^\circ$ in alcohol. Similar compounds of gallic acid with α -methylglucoside and glycerol, and of *p*-hydroxybenzoic acid with dextrose are also described.

Manning and Nierenstein (Ber. 1912, 45, 1546) considered that a sugar nucleus is not present in pure gallotannin, and point out that this is not produced when either Schering's tannin or Herzig and Renner's methyl tannin (*l.c.*) is hydrolysed with alkali. Again, ethyl gallate is the sole product of the esterification of this tannin.

Herzig (Ber. 1912, 45, 1985) considers that the argument of these authors is no proof of the absence of a sugar nucleus in methyl tannin or tannin itself, whereas Biddle and Kelley (J. Amer. Chem. Soc. 1912, 34, 918) show that the so-called ethyl tannate of Manning is in reality ethyl gallate. On the other hand, Feist reiterated the fact (Ber. 1912, 45, 1493) that in 1908 (Chem. Zentr. 1908, ii. 1352) he isolated *glucogallic acid*, a compound of gallic acid and glucose, from Turkish gall-nuts.

Fischer and Freudenberg (Ber. 1912, 45, 2709) further supported their view that gallotannin is a pentadigalloyl-glucose, and in continuation of their syntheses of tannin compounds employed pentamethyl-*m*-digalloyl chloride with interesting results. Whereas the digallic acid previously synthesised by these authors is the *p*-compound (Ber. 1910, 43, 628), gallotannin is derived from the *m*-acid, for Herzig has shown that methyl tannin, when hydrolysed, gives gallic acid trimethyl ether and 3 : 4 gallic acid dimethyl ether (*cf.* also Nierenstein).

When the trimethyl ether of galloyl chloride reacts with 3 : 4 gallic acid dimethyl ether, according to the method employed by these authors, *pentamethyl-m-digallic acid*—



m.p. 192° – 193° , is produced (*cf.* Mauthner, Ber. 1905, 38, 389; Monatsh. 1909, 30, 543), and from this the chloride, m.p. 109° – 110° , is readily obtained. In the presence of quinoline, this is condensed with α - and β -glucose respectively, and such a procedure was adopted, because it was found that benzoyl and cinnamyl chlorides, in a similar manner, give with α - and β -glucose stereo-isomeric compounds.

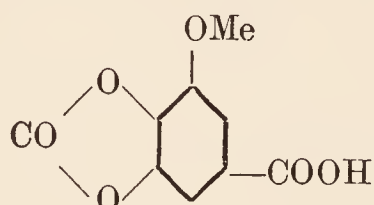
The *m*-digalloyl derivatives thus prepared are amorphous, possess the composition of penta-[pentamethyl-digalloyl]-glucose, but appear in each case to be a mixture of stereo-isomerides. Thus the α -glucose product in acetylene tetrachloride had $[\alpha]_D + 28^\circ$ (approx.), and after repeated solution in hot alcohol $[\alpha]_D + 14^\circ$ (approx.), whereas the β -glucose compound $[\alpha]_D + 19.5^\circ$ behaved similarly.

In case gallotannin is penta-*m*-digalloyl-glucose it is evident that this product will represent its methyl ether, and indeed a very close resemblance appears to exist between this substance and the preparation of Herzig. The methyl ether prepared from natural tannin (Herzig, *l.c.*) is not a uniform substance, but

probably also a mixture of stereo-isomerides, the sample employed having in acetylene tetrachloride $[\alpha]_D^{26} + 14^\circ$, and after repeated solution in acetone and methyl alcohol $[\alpha]_D^{21} + 10.6^\circ$. Finally, the criticisms of Manning and Nierenstein (*l.c.*) as to the absence of glucose in pure tannin are shown to be valueless, and the elaborate results of Nierenstein are difficult to comprehend.

Nierenstein (Ber. 1914, 47, 891) has withdrawn his criticism of Fischer's proposals concerning the structure of tannin, and from the behaviour of tannin with yeast now concludes that glucose is an essential constituent of tannin.

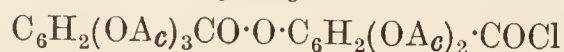
A summary of the position of the chemistry of tannin has been published by Fischer (Ber. 1913, 46, 3253), whilst further steps towards the synthetic production of tannin products have also been taken by him. These include the development of an improved process for the preparation of *m*-digallic acid in quantity (Fischer and Freudenberg, Ber. 1913, 46, 1116). To this end gallic acid was converted into carbonyl-gallic acid, $\text{CO} \begin{smallmatrix} \diagup \text{O} \diagdown \end{smallmatrix} \text{C}_6\text{H}_2(\text{OH})\text{COOH}$, by the action of carbonyl chloride, in the presence of alkali or pyridine, and from this the methyl derivative was produced which has the structure—



This product readily condenses with tricarbomethoxy-galloyl chloride in alkaline solution, and by removal of the carbonic acid residues from the resulting product, a yield of over 50 p.e. of *m*-digallic acid may be obtained.

A still further improved method of preparing *m*-digallic acid is described by Fischer, Bergmann and Lipschitz (Ber. 1918, 51, 45). This consists in condensing 3·5-diacetyl-gallic acid with triacetyl-galloyl chloride to give penta-acetyl-*p*-digallic acid. The latter, when cautiously hydrolysed by cold dilute ammonia solution, gives *m*-digallic acid, the reaction being due to the wandering of an acetyl group during the hydrolysis. By this method it was found possible to obtain both the meta- and para-penta-acetyl-digallic acids in a pure condition, a fact which subsequently permitted of the preparation of penta-digalloylglucose by Fischer and Bergmann (Ber. 1918, 51, 1760). Penta-(*m*-digalloyl)- β -glucose was shown to be remarkably similar to Chinese tannin, differing only by its specific rotation in aqueous solution, which, owing to the colloidal nature of the latter, they do not consider to be of importance.

Penta-acetyl-m-digalloyl chloride



six-sided plates, m.p. 180° (corr.), is formed by the action of phosphorus pentachloride on acetyl-*m*-digallic acid in the presence of chloroform, from which, by the action of methyl alcohol in the presence of quinoline, methyl penta-acetyl-*m*-digallate is obtained, m.p. 167° —

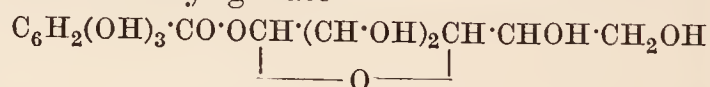
168° (corr.). With β -glucose it yields (penta-acetyl-*m*-digalloyl)- β -glucose



specimens of which gave $[\alpha]_D^{18} + 3.79^\circ$ and $[\alpha]_D^{15} + 2.60^\circ$ in 's'-tetrachlorethane. The corresponding *p*-compound similarly prepared has in the same solvent $[\alpha]_D^{13} + 1.54^\circ$. By deacetylation with cold aqueous sodium hydroxide at 0° , and purification by means of its potassium salt, penta-(*m*-digalloyl)- β -glucose is obtained, and this closely resembles Chinese tannin. The preparation of similar α -glucose derivatives is also described which differ from the β -glucose compounds merely by their specific rotation.

The same investigators (Ber. 1919, 52, (B) 829) have subsequently shown that the deacetylating of these acetyl-galloyl-glucose compounds can be effected at the ordinary temperature by the employment of methyl alcoholic hydrochloric acid, and that in this way penta-*m*-digalloyl α - and β -glucoses can be obtained in a purer condition. Chinese tannin, penta-digalloyl α - and β -glucose have respectively in water $[\alpha]_D + 46.3^\circ$, $+56.6^\circ$, and $+33.7^\circ$.

Penta-(triacetyl-galloyl)- α - and β -glucoses are also described, and from these it has been possible to synthesise the penta-galloyl derivatives of α - and β -glucose. The *l*-galloyl- β -glucose obtained from aceto-bromo-glucose and silver tri-acetyl-gallate



has proved to be identical with the glucogallin isolated by Gilson from Chinese rhubarb (Compt. rend. 1903, 136, 385).

Iljin considers Chinese tannin to be a mixture (Ber. 1914, 47, 985), but Freudenberg and Szalasi (Ber. 1922, 55, (B) 2813), whilst confirming his experiments, conclude that it is fundamentally homogeneous, the difference in specific rotation shown by the various fractions in aqueous solution being due, in reality, to their colloidal character. Thus in other solvents the rotation of these fractions is shown to be identical. Herzig points out (Ber. 1923, 56, (B) 221) that the methylotannin obtained by the action of diazo-methane on Chinese tannin (*cf.* Herzig and Tscherne, *see above*) is a homogeneous compound. On the other hand, Karrer, Salomon and Peyer (Helv. Chim. Acta, 1923, 6, 3) find that Chinese tannin is not a uniform substance, for, by precipitation with aluminium hydroxide, fractions of very different rotatory power can be obtained. From the higher rotating fractions they have prepared *l*-bromo-tetragalloyl-glucose and *l*-bromo-tetra-(triacetyl-galloyl)-glucose ($[\alpha]_D + 59.5^\circ$ in acetone), whereas from the lower rotating fractions, *l*-bromo-tetra-(triacetyl-galloyl)-glucose of varied rotating power and other similar derivatives were obtained. As a result they consider that Chinese tannin is a mixture of closely related galloylated glucoses.

A gallotannin derived from Chinese galls and apparently free from glucose has been described by Mitchell (Analyst, 1923, 48, 5), and his results have been confirmed by Nierenstein (Ber. 1923, 1876).

For further references to gallotannin, *see*

Harnack (Arch. Pharm. 1896, 234, 537), colour reaction; Ljubavin (J. Russ. Phys. Chem. Soc. 1901, 33, 680), tannin and tartar emetic; Thibault (Bull. Soc. Chim. 1903, [iii.] 29, 745), tannin and bismuth; Vigneron (J. Pharm. Chim. 1906, [vi.] 23, 469), iodotannin; Farberwerke vorm. Meister, Lucius, and Brüning (D. R. P. 173729), mixed anhydrides of tannic and cinnamic acids; Biginelli (Gazz. chim. ital. 1907, 37, ii. 205; *ibid.* 1903, 38, i. 559), tannates of quinine; Hildebrandt (D. R. P. 188318), tannin and formaldehyde; Francis and Nierenstein (Collegium, 1911, 335), action of benzoyl chloride and potassium cyanide on benzoyl-hydroxybenzoic acids and on acetylated hydroxybenzoylhydroxybenzoic acids; Nierenstein (Die Gerbstoffe); Nierenstein, Spiers and Gieke (Chem. Soc. Trans. 1921, 119, 275), and Nierenstein (J. Soc. Chem. Ind. 1922, 41, 291).

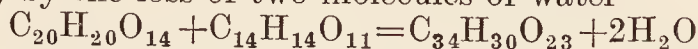
Chestnut tannin.—Chestnut tannin has been examined by Nass (Inaugural Diss. 1884, Dorpat, Russia) and by Trimble (The Tannins, ii. 119). According to the latter author it is probably identical with ordinary gallotannin (see CHESNUT EXTRACT).

Chebulinic acid or Eutannin.—This tannin was isolated by Fridolin from myrobalans, *Terminalia chebula* (Retz.), which also contain an ellagitannin. It crystallises in rhombic prisms, is sparingly soluble in cold water, gives with ferric chloride a blue-black precipitate, and by heating with water is converted into gallic acid and a new tannin.

Thoms (Chem. Zentr. 1906, i. 1829; Apoth. Zeit. 1906, 21, 354) found that commercial *eutannin* is identical with chebulic acid $C_{28}H_{22}O_{19}$. It consists of small colourless needles, containing water of crystallisation, reacts acid to litmus paper, decomposes at 234° , and has $[\alpha]_D$ initially $+61.7^\circ$, gradually rising to $+66.9^\circ$. An *ennea-acetyl* and *methyl* derivative are described, the latter giving trimethylgallic acid by the action of sodium hydroxide solution. With water at 100° – 150° the tannin yields gallic acid and *eutannin hydrate* $C_{28}H_{24}O_{20}$, a colourless powder decomposing at 200° – 210° . When eutannin is dissolved in cold sodium hydroxide, the solution acidified with acetic acid, and then treated with lead acetate solution, the resulting precipitate, after decomposition with sulphuretted hydrogen, gives gallic acid, and a tannin $C_{14}H_{16}O_{12}$ or $C_{14}H_{14}O_{11}$, which consists of a yellow powder, having $[\alpha]_D +26^\circ$ at 15° , and giving a blue coloration with ferric chloride. According to Fischer and Freudenberg (Ber. 1912, 45, 915), when hydrolysed chebulinic acid gives also dextrose (see also Ber. 1918, 51, 298).

Freudenberg (Ber. 1919, 52, (B) 1238), by heating chebulinic acid with water has obtained gallic acid, a crystalline tannin (a), and a phenol carboxylic acid $C_{14}H_{14}O_{11}$ (b). This latter, which has $[\alpha]_D^{20} +34^\circ (\pm 4)$, is dibasic, gives a brucine salt, melting at about 250° , and, when distilled under reduced pressure, yields pyrogallol. The crystalline tannin, which has a specific rotation in alcohol of $[\alpha]_D^{18} +85^\circ (\pm 4)$, is evidently a digalloyl-glucose, and this has been confirmed by Freudenberg and Fick (Ber. 1920, 53, (B) 1828) by the preparation of di-

(*triacyl-galloyl*) *triacyl-glucose*, needles, m.p. 177° – 179° . It is probably a derivative of α -glucose. Chebulinic acid, which is now shown to be $C_{34}H_{30}O_{23}$, and not $C_{28}H_{22}O_{19}$, as was formerly suggested, is apparently derived from the di-galloyl-glucose (a) and the acid $C_{14}H_{14}O_{11}$, (b) by the loss of two molecules of water



Hamamelitannin.—This compound, another of the few gallotannins as yet isolated in a crystalline condition, occurs in the bark of the *Hamamelis virginiana* (Linn.), a tree 10 to 12 ft. high, common in North America. The bark, previously extracted with light petroleum to remove plant wax, is exhausted with ether-alcohol (5:1), the solution evaporated, the residue dissolved in a little alcohol and treated with ether to precipitate certain impurities. Evaporation of the ethereal liquid gives a product, a hot aqueous solution of which, after treatment with alumina and animal charcoal, deposits, on cooling, the substance in the form of small colourless needles. From a dilute aqueous solution, hamamelitannin $C_{14}H_{14}O_9$, crystallises with $5H_2O$, but deposited from strong solutions the crystals contain $2\frac{1}{2}H_2O$. The air-dried substance melts at 115° – 117° , although when dried at 100° the m.p. is 203° . Hydrolysed with boiling dilute sulphuric acid, gallic acid only was produced, and the presence of a sugar could not be detected. Hamamelitannin is dextro-rotatory, $[\alpha]_D = +35.43^\circ$.

Benzoylhamamelitannin $C_{14}H_9O_9(C_7H_5O)_5$ is a yellow powder which melts at about 125° – 132° (Grüthner, Arch. Pharm. 236, 303). According to Fischer and Freudenberg (Ber. 1912, 46, 2712), however, this tannin probably contains a sugar nucleus.

Freudenberg (Ber. 1919, 52, (B) 177) has subsequently obtained an amorphous methyl derivative of hamamelitannin by means of diazo-methane in acetone solution. This, on hydrolysis with *N* sodium hydroxide, gives gallic acid tri-methyl-ether. By hydrolysing an aqueous solution of the tannin covered with toluene by means of *tannase* (see Freudenberg and Vollbrecht, Zeitsch. physiol. Chem. 1921, 116, 277), it gives gallic acid and a lævo-rotatory sugar, in quantities corresponding to the constitution of a di-galloyl-hexose. According to Freudenberg and Peters (Ber. 1920, 53, (B) 953) the sugar thus obtained is probably an aldo-hexose.

Oak wood tannin is probably a member of this group, but is described under the heading of *Phlobatannins*.

Acertannin.—Acertannin exists in the leaves of the *Acer ginnala* (Korean maple tree), a plant which is common throughout Korea. The leaves are plucked during mid-autumn, and are exported to China, where they are extensively used for the black dyeing of cotton.

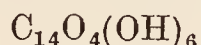
For the isolation of the tannin Perkin and Uyeda (Chem. Soc. Trans. 1922, 121, 67) employ a concentrated alcoholic extract of the air-dried leaves. This is diluted with water, the mixture freed from chlorophyll and wax by means of ether, and the tannin then isolated with ethyl acetate in the usual manner. The product digested with twice its volume of boiling water becomes semi-solid, owing to the separation of crystals of accertannin, whereas a more soluble amorphous tannin remains in solution.

ellagitannin itself in the character of their sugar nuclei will be later discovered.

Though various hydroxydiphenylmethyloid compounds have been synthetically prepared, e.g. metellagic acid $C_{15}H_5O_4(OH)$, catellagic acid $C_{14}H_4O_4(OH)_2$, flavellagic acid



and coeruleoellagic (cyanellagic) acid



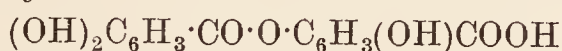
(*l.c.*), ellagic acid is the only member of this group which has been isolated from natural sources.

Pomegranate tannin $C_{20}H_{16}O_{13}$ is an amorphous greenish-yellow substance contained in the root bark of *Punica granatum* (Linn.). Boiling dilute sulphuric acid hydrolyses it with formation of a sugar and ellagic acid (Rembold, *Annalen*, 143, 385).

Knopfern-tannin is obtained from galls produced by the *Cynips calcicis* on the immature acorns of various oaks, principally the *Q. cerris* of the Slavonian plains. Löwe (*Zeitsch. anal. Chem.* 1875, 13, 46) considers the tannin to be identical with gallotannin, but Nierenstein (*Chem. Soc. Trans.* 1919, 115, 1174), who obtains by hydrolysis dextrose and ellagic acid, concludes that it is derived from luteoic acid and dextrose.

GROUP III.—CATECHOL OR PHLOBATANNINS.

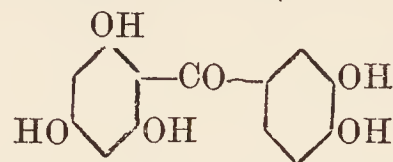
The catechol tannins are characterised among other distinctive features by the important fact that when digested with boiling dilute mineral acids a red precipitate, known as 'anhydride' or 'phlobaphene,' is produced. The designation 'catechol' arises from the fact that the majority of these substances give a green coloration with ferric chloride, and protocatechuic acid or catechol as one of their decomposition products. Such a classification is, however, misleading, in that by comparison with gallotannin, one is led to infer that these substances are similarly constituted and derived from diprotocatechuic acid only—



When hydrolysed, however, diprotocatechuic acid gives two molecules of protocatechuic acid without production of phlobaphene (Emil Fischer, private communication). Moreover, certain phlobaphene-yielding compounds are now known to exist in which a catechol nucleus is absent. Thus the cyanomaclurin of Jakwood (*q.v.*) is an instance in point, for although it contains only phloroglucinol and resorcinol nuclei, it readily yields a red anhydride of this character (*cf.* also Mimosa tannin, Pistachia tannin, and Maletto tannin). Evidently therefore the phlobaphene reaction is either due to the special structure of the tannin itself, or to the presence of a second phenolic grouping other than catechol in the molecule. This structure may perhaps vary in certain cases, but until this is clear it appears to be preferable to include all phlobatannins under one group rather than to complicate the subject by the introduction of subdivisions.

Böttger and Etti (*l.c.*) have suggested a benzophenone structure for certain tannins, and

this applied to the phlobatannins has, at first sight, the merit that *maclurin* (*see* OLD FUSTIC)—



with dilute hydrochloric acid gives rufimoric acid (Wagner, *Jahres*. 1851, 420), a red amorphous phlobaphene-like mass. *Kinoïn* (*see* Kino), usually regarded as the methyl ether of a penta-hydroxybenzophenone, is readily transformed into kino-red, whereas *aromadendrin* (*see* Kino), apparently also a benzophenone derivative, resembles, according to Maiden and Smith, *catechin* in many of its properties. It has not yet been ascertained if the carboxylic acids of certain hydroxybenzophenones are tannins, but on the other hand it is to be remembered that compounds possessing such a structure will be strong mordant dye-stuffs, a property which is generally absent from tannins of the so-called catechol type. As already indicated, many phlobatannins are known which contain two distinct nuclei, more frequently phloroglucinol in addition to catechol, a fact which in these cases accounts for their reactivity with diazo-benzene. All phlobatannins can apparently be precipitated from their aqueous solutions by means of bromine, a property which may also be accounted for in part by the presence of a phloroglucinol or resorcinol grouping therein. On the other hand, numerous phlobatannins appear to exist in which such a reactive phenolic nucleus is absent, and it may be thus presumed that in these cases, at least, the reaction is of an additive character, and due to unsaturation.

It is most probable that the phlobaphene reaction is, in many cases, to be assigned to the well-known reactivity of the phloroglucinol group present in these substances, and this has also been suggested by Emil Fischer. Thus coloured compounds can be obtained by the interaction of phloroglucinol with many aldehydes, of which the red phloroglucinol vanillein is an example, and moreover the phloroglucides of Couder (*Ber.* 1895, 28, 26), prepared by passing hydrogen chloride into mixtures of phloroglucinol and various sugars in aqueous solution, are coloured, the *d*-galactose phloroglucide possessing a red tint. Again, by boiling dextrose and phloroglucinol with dilute hydrochloric acid, a brownish-red precipitate of a phlobaphene-like character can be easily produced (private communication). Interesting in this respect also is the 'phlorotannin red' of Schiff (*Annalen*, 245, 40), which he obtained by heating his so-called diphoroglucinol carboxylic acid to 160°–175°.

That phlobatannins like gallotannin owe their tanning property, as a rule, to the depside grouping appears likely, and it has indeed been observed by Trimble (*The Tannins*, ii. 91) that tannins from various species of oak, on long digestion with boiling 2 p.c. hydrochloric acid, give not only phlobaphene but some quantity of protocatechuic acid.

In the light of the researches of E. Fischer and Freudenberg (*l.c.*), it is also to be anticipated that many of these compounds will be eventually found to possess a sugar nucleus.

Closely connected with the phlobatannin

group are the well-defined crystalline substances catechin, aca-catechin and cyanomacclurin.

Catechin, although not a tannin, reacts with pine wood and hydrochloric acid, gives with bromine water the insoluble bromcatechuratin and readily yields substances of a phlobaphene character. Though the evidence is not precise it is stated by Loewe and also by Etti that catechin can be readily transformed into catechutannic acid, a substance existing side by side with it in the plant and possessing properties typical of the phlobatannin group. It has indeed been suggested that the catechol tannins of certain plants may owe their origin to the prior existence of substances of the catechin type, and that in addition to the compounds previously enumerated, the so-called quebracho resin and guarana catechin are intermediate products of tannin formation. Again, according to Procter (private communication), a colourless catechin-like substance is to be found in mangrove cutch.

With the exception of coca-tannic acid, no crystalline catechol tannins have been described. They are very similar in appearance to natural gallotannin, but on keeping, especially in the moist condition, are apt to develop a red tint. According to Perkin, most phlobatannins can be prepared in a nearly colourless condition by extracting a solution of the crude tannin to which sodium bicarbonate has been added with ethyl acetate (*cf.* *Gallotannin*).

Numerous phlobatannins have been isolated, and a description of them is given below, although it is extremely doubtful whether the majority of these are individuals. In many cases, indeed, the general reactions of these compounds are the same, and considering the extreme difficulty in the effective purification of amorphous preparations of this character, specific differences which have been observed will no doubt, on further investigation, largely disappear. Trimble (*l.c.* ii. 132), who submitted certain phlobatannins to careful purification, found that there was a fair approximation in their percentage compositions, and it is thus natural to presume that the known members of this group are not so numerous as was formerly considered to be the case.

Anachueta wood and bark contain a tannin which gives a green coloration with iron salts.

Aspertannic acid $C_{14}H_{16}O_8$ was obtained by Schwarz from Woodruff (*Asperula odorata*, Linn.), and gives a green colour with ferric salts. It does not yield precipitates with albumen, gelatin, and tartar emetic solutions.

Atherospermatannin, from the bark of *Atherosperma moschatum* (Labill.), gives a green colour with ferric salts. A lead salt



has been described by Zeyer (Jahrb. Min. 1861, 769).

Barbitamao-tannic acid, from the bark of the *Stryphnodendron barbatimum* (Mart.), (Wilbuszwitz, Ber. Ref. 1886, 19, 349), is an amorphous red powder, which yields a phlobaphene, and on fusion with alkali, *protocatechuic acid* and *phloroglucinol*.

Beech tannin, from the bark of the red beech, contains a tannin of the composition $C_{20}H_{22}O_9$ (Etti, Monatsh. 10, 650).

Caffetannic acid $C_{15}H_{18}O_9$ occurs in coffee berries in the form of calcium and magnesium

salts (Rochleder, Annalen, 59, 300); in cainia root, *Chiococca brachiata* (Ruiz. et Pav.), (Rochleder and Hlasiwetz, *ibid.* 1848, 66, 35); *Nuxvomica* (Sander, Arch. Pharm. 1897, 235, 133); St. Ignatius beans (*ibid.*), and Paraguay tea, *Ilex paraguayensis* (A. St. Hill.), (Rochleder, Annalen, 1847, 66, 39), (*cf.* also Graham, Stenhouse and Campbell, J. pr. Chem. 1856, 69, 815; Arata, Ber. 1881, 14, 2251; Kunz-Krause, Arch. Pharm. 1893, 231, 613; Ber. 1897, 30, 1617).

It is an amorphous powder readily soluble in water, gives a dark green coloration with ferric chloride, and when boiled with potassium hydroxide solution gives *caffeic acid* and a sugar (Hlasiwetz, Annalen, 1866, 142, 220), which is glucose (Sander, *l.c.*). On dry distillation *catechol* is formed, and by fusion with alkali *protocatechuic acid* is obtained. The ammoniacal solution becomes green on exposure to air with formation of *viridic acid*, a substance which is also present in coffee berries in the form of its calcium salt (Rochleder, Annalen, 63, 197). According to Griebel (Inaugural Diss. Munich, 1903) caffetannic acid is $C_{18}H_{24}O_{10}$, and a penta-acetyl derivative corresponding to this formula is described.

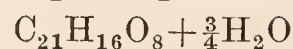
Callutannic acid $C_{14}H_{14}O_9$ contained in heather, *Calluna vulgaris* (Salisb.), is an amber-coloured substance. It gives a green coloration with ferric chloride, and when heated with dilute mineral acids yields an amorphous anhydro derivative $C_{14}H_{10}O_7$ (Rochleder, Annalen, 84, 354; Sitz. Ber. 9, 286).

Canaigre tannin is present in the tuberous roots of the *Rumex hymenosepalus* (Torr.), an important American tanning material. It has been submitted to an elaborate examination by Trimble (The Tannins, 1894, ii. 115), who describes it as a yellowish-white powder readily soluble in water, which gives with lead acetate solution a yellow precipitate, and with ferric chloride a green precipitate. It reacts with bromine water to give a yellow deposit, and on heating to 160°–190° is decomposed with production of *catechol*. Boiling 2 p.c. hydrochloric acid yields an insoluble red phlobaphene together with some *protocatechuic acid*. Sugar is not formed in this decomposition. Analysis gave C=58.10; H=5.33, figures which approximate to, though they are somewhat lower than, those given by the best-known phlobatannins.

Catechutannic acid (see CATECHU).

See also J. G. and B. L. de G. Peacock, Amer. J. Pharm. 1923, 95, 613–623.

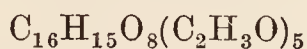
Cherry bark tannin $C_{21}H_{20}O_{10} + \frac{1}{2}H_2O$ is present in the bark of the *Prunus cerasus* (Linn.), (Rochleder, Sitz. Ber. 59, 819), and gives a green coloration with ferric chloride. It is not a glucoside, but when digested with boiling dilute acids gives a red phlobaphene



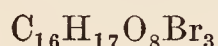
Cocatannic acid $C_{17}H_{22}O_{10} + 2H_2O$ (?), present in the leaves of the *Erythroxylon coca* (Linn.) (Niemann, Jahrb. Min. 1860, 386), is sparingly soluble in cold water and gives a green coloration with ferric salts. According to Warden (Pharm. J. 18, 985) it can be obtained in microscopic crystals of a sulphur yellow colour.

Colatannin or *Kolatannin* $C_{16}H_{20}O_8$, a light red amorphous powder, exists in the Kola nut,

Cola acuminata (Schoot and Endl.), in combination probably with caffeine and theobromine (Knox and Prescott, Amer. Chem. J. 1897, 19, 63) With ferric acetate it gives a green coloration, and on fusion with alkali *protocatechuic acid* is obtained. *Penta-acetylkolatannin*



colourless powder, *tribromokolatannin*



red-brown powder, *penta-acetyl-tribromokolatannin* $\text{C}_{16}\text{H}_{12}\text{O}_8\text{Br}_3(\text{C}_2\text{H}_3\text{O})_5$, *pentabrom*, and *hexabromokolatannin* have been described. On heating, kolatannin yields various anhydrides $(\text{C}_{16}\text{H}_{19}\text{O}_7)_2\text{O}$ at $107^\circ\text{--}110^\circ$, $(\text{C}_{16}\text{H}_{17}\text{O}_6)_2\text{O}$ at $135^\circ\text{--}140^\circ$, and $\text{C}_{16}\text{H}_{16}\text{O}_6$ at $155^\circ\text{--}156^\circ$.

Cortepinitannic acid $\text{C}_{32}\text{H}_{34}\text{O}_{17}$ occurs together with pinicortannic acid in the bark of the Scotch fir, *Pinus sylvestris* (Linn.). It consists of a bright red powder, the aqueous solution of which gives an intense green coloration with ferric chloride (Kawaler, Sitz. Ber. 11, 363).

Euphrasia tannin is present according to Enz (Vierteljahrsh. Pharm. J. 8, 175) in the green parts of *Euphrasia officinalis* (Linn.), and gives a green colour reaction with ferric salts. Its lead salt has the composition $\text{C}_{32}\text{H}_{20}\text{Pb}_3\text{O}_{20}$.

Fragarianin, v. *Strawberry tannin*.

Filitannic acid $\text{C}_{41}\text{H}_{36}\text{NO}_{18}$ (?) exists in fern-root (*Aspidium filix mas*, Swartz) (Malin, Annalen, 143, 276), and forms a red-brown powder which, in aqueous solution, gives an olive-green coloration with ferric chloride. By boiling with dilute sulphuric acid it gives *filix red* $\text{C}_{20}\text{H}_{18}\text{O}_{12}$, an amorphous compound, and this when fused with alkali gives *phloroglucinol* and *protocatechuic acid* (cf. also Reich, Arch. Pharm. 1900, 238, 648).

Fraxitannic acid $\text{C}_{26}\text{H}_{32}\text{O}_{14}$ (?) occurs in the leaves of the ash tree, *Fraxinus excelsior* (Linn.). It consists of a brownish-yellow deliquescent powder, and when heated at 100° loses water and forms an almost insoluble anhydride $\text{C}_{26}\text{H}_{30}\text{O}_{13}$ (Gintl and Reinitzer, Monatsh. 3, 745). Aqueous ferric chloride produces a dark green coloration, and when oxidised with permanganate this tannin yields quinone. *Acetylfraxitannic acid* $\text{C}_{26}\text{H}_{28}\text{O}_{14}(\text{C}_2\text{H}_3\text{O})_4$, *benzoylfraxitannic acid* $\text{C}_{26}\text{H}_{28}\text{O}_{14}(\text{C}_7\text{H}_5\text{O})_4$, *tribromofraxitannic acid* $\text{C}_{26}\text{H}_{29}\text{Br}_3\text{O}_{14}$, and *tetra-acetyltribromofraxitannic acid* $\text{C}_{26}\text{H}_{25}\text{Br}_3\text{O}_{14}(\text{C}_2\text{H}_3\text{O})_4$ have been described.

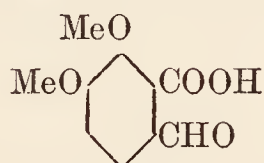
Galitannic acid $\text{C}_{14}\text{H}_{16}\text{O}_{10}\cdot\text{H}_2\text{O}$ exists in the bark of the *Galium verum* (Linn.) (Schwarz, Annalen, 83, 57). It gives a yellow precipitate with basic lead acetate and a green colour reaction with ferric chloride.

Guarana tannin is present in the *Paullinia cupana* (H. B. and K.), the seeds of which, known as 'guarana,' contain theine and are extensively used in South America for medicinal purposes. According to Nierenstein (Die Gerbstoffe, 20) the tannin consists of small colourless crystals, m.p. $199^\circ\text{--}201^\circ$, and yields an acetyl derivative, m.p. $134^\circ\text{--}136^\circ$. It is lævo-rotatory, having $[\alpha]_D^{20} = -72.4^\circ$ in water, and $[\alpha]_D^{20} = -39.1^\circ$ in alcohol.

Hemlock tannin $\text{C}_{20}\text{H}_{18}\text{O}_{10}$ (?) is present in Hemlock bark, *Tsuga* [*Abies*] *canadensis* (Carr.), the extract of which is prepared on a very large scale in North America for tanning purposes.

According to Böttiger (Ber. 1884, 17, 1125), it is probably related to the quercitannic acid of the oak, and on heating with sulphuric or hydrochloric acid gives the anhydride *hemlock red* $\text{C}_{40}\text{H}_{30}\text{O}_{17}$. With hydrochloric acid at 180° , hemlock red evolves methyl chloride; when heated with acetic anhydride the acetyl compound $\text{C}_{40}\text{H}_{23}\text{O}_{17}(\text{C}_2\text{H}_3\text{O})_7$ is produced, whereas bromine gives a mixture of the compounds $\text{C}_{40}\text{H}_{20}\text{Br}_{10}\text{O}_{17}$ and $\text{C}_{40}\text{H}_{16}\text{Br}_{14}\text{O}_{17}$. Bromine added to the diluted tannin extract precipitates *tetrabromhemlock tannin*, $\text{C}_{20}\text{H}_{14}\text{Br}_4\text{O}_{10}$, a yellow powder which yields the *penta-acetyl* derivative $\text{C}_{20}\text{H}_9\text{Br}_4\text{O}_{10}(\text{C}_2\text{H}_3\text{O})_5$, and by the further action of bromine the bromine compound $\text{C}_{20}\text{H}_{12}\text{Br}_6\text{O}_{10}$ (cf. Trimble, Amer. J. Pharm. 1897, 69, 354, 406; J. Soc. Chem. Ind. 1898, 17, 558) is produced.

Manning and Nierenstein (Chem. Soc. Trans. 1919, 115, 662) give details of the preparation of hemlock tannin. According to these authors the methylated tannin, when hydrolysed, yields veratric acid and opianic acid



whereas from the free tannin the products of hydrolysis appeared to consist of protocatechuic and 2:3 dihydroxybenzoic acids.

Hop tannin $\text{C}_{22}\text{H}_{26}\text{O}_9$, present in hops (*Humulus lupulus*, Linn.) (Etti, Annalen, 180, 223; Monatsh. 10, 651), has all the properties of a catechol tannin. It gives with ferric chloride a dark green coloration and with boiling dilute mineral acid the phlobaphene 'hop red' $\text{C}_{38}\text{H}_{26}\text{O}_{15}$. Hop red forms a cinnamon-coloured powder and on fusion with potash yields *phloroglucinol* and *protocatechuic acid*.

Horse chestnut tannin $\text{C}_{26}\text{H}_{24}\text{O}_{12}$ is present in nearly all parts of the *Æsculus hippocastanum* (Linn.) and in the root bark of the apple tree (Rochleder, Sitz. Ber. 53, [ii.] 478; 54, [ii.] 609). It consists of a nearly colourless powder, the solution of which gives a green coloration with ferric chloride, and when boiled with dilute mineral acid the phlobaphene $\text{C}_{26}\text{H}_{22}\text{O}_{11}$ or $\text{C}_{26}\text{H}_{20}\text{O}_{10}$. On fusion with alkali, *phloroglucinol* and *protocatechuic acid* are produced. V. also *phyllæscitannin* and CHESTNUT EXTRACT.

Ipecacuanhic acid $\text{C}_{14}\text{H}_{18}\text{O}_7$ was obtained by Willigk (Annalen, 76, 345) from the roots of *Psychotria ipecacuanha* (Stokes), and consists of a reddish-brown, bitter hygroscopic substance. Its solution gives a green coloration with ferric chloride.

Japonic acid (see CATECHU).

Kino (see KINO).

Larch tannin.—The bark of the larch, *Larix europæa* (DC.), contains considerable quantities of a tannin which was examined by Stenhouse (Phil. Mag. 23, 336). It forms an olive-green precipitate with ferric salts, and when boiled with dilute sulphuric acid a red phlobaphene is produced.

Maletto tannin occurs in the bark of *Eucalyptus occidentalis* (Endl.) and other species of eucalyptus. According to Strauss and Geschwender (Zeitsch. angew. Chem. 1906, 19, 1121) it possesses the formula $(\text{C}_{43}\text{H}_{50}\text{O}_{20})_2$, and appears to be identical with quebracho tannin. Dekker (Arch. Néerland. 1909, ii. 14, 50) prefers

the formula $(C_{19}H_{20}O_9)_n$, and describes the acetyl derivative $C_{38}H_{28}O_{17}Ac_{10}$ and benzoyl derivative $C_{19}H_{15}O_{12}Bz_5$. Heated with zinc dust and sodium hydroxide solution the tannin gives small quantities of *gallic acid* and *phloroglucinol*, whereas dry distillation yields *pyrogallol* and traces of other phenols. Boiling dilute sulphuric acid forms 'maletto red' $C_{57}H_{50}O_{22}$, from which the acetyl derivative $C_{57}H_{35}O_{22}Ac_{15}$ can be obtained.

Mangrove tannin $C_{24}H_{26}O_{12}$.—This important tannin is derived from the *Rhizophora mangle* (Linn.), *R. mucronata* (Lam.), *Ceriops candolleana* (Arn.), *C. roxburghiana* (Arn.), and other allied species. It is described as an amorphous red powder, which on fusion with alkali gives *protocatechuic acid*, and with boiling dilute sulphuric acid the phlobaphene $C_{48}H_{46}O_{21}$. The monacetyl derivative $C_{24}H_{25}O_{12}(C_2H_3O)$ melts at 205° (Nierenstein, Die Gerbstoffe). This tannin closely resembles in its properties catechutannic acid (see CATECHU), and indeed mangrove cutch and catechu may be employed in many cases for the same purpose. Possibly these two substances are identical, and Procter (private communication) has isolated from mangrove cutch a small quantity of a colourless crystalline substance resembling catechin. Perkin, who examined an ethyl acetate extract of the fresh bark of the *C. candolleana*, prepared in Borneo, was unable to detect the presence of a catechin, but obtained the tannin as a pale yellow powder, which gave a green coloration with ferric chloride solution, and resembled catechutannic acid in many respects.

Mimosa tannin is derived from various species of *Mimoseæ*, such as the *Acacia arabica* (Willd.) of Egypt, the so-called 'Wattles' of Australia, and numerous others. The tannin present is interesting in that though it possesses the reactions of a phlobatannin, such as phlobaphene production, precipitation by bromine water and solubility of its lead compound in acetic acid, &c., it gives a bluish-violet coloration with ferric chloride. Ammonium sulphide gives a precipitate with a mimosa solution, when after removal of the excess by boiling, a few drops of sulphuric acid are added, followed by a small quantity of salt. All other phlobatannins, except Maletto and Pistaschia tannins, give no precipitate by this method (Stiasny, private communication).

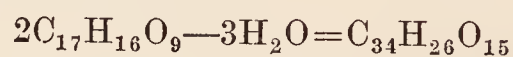
Moritannic acid, see *Maclurin*.

Oxypinitannic acid, v. *Pinitannic acid*.

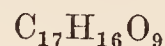
Oak bark tannin or *Quercitannic acid* is found in the bark of the oak, and is not to be confused with the tannin of oak-wood from which it is distinct, and which is described below under the name of quercinic acid. In 1792 George Swayne communicated to the Society of Arts his results on the use of oak leaves in tanning (Trimble, The Tannins, ii. 51), and the subject was again discussed by Berzelius in his Lehrbuch, 1827, and by Liebig (Handbuch der Chemie, 1843). Assumed at that time to be identical with the tannin of nut-galls (gallotannin), it was first shown by Stenhouse (Phil. Mag. 22, 425) to differ from this substance. According to Grabowski (Sitz. Ber. 56, [ii.] 388), Oser (*ibid.* 72, [ii.] 178), Johanson (Arch. Pharm. [iii.] 9, 210), Bötttinger (Ber. 14, 1598), quercitannic acid is in reality a glucoside, but Etti (Ber. 14, 1826; Monatsh. 4, 512) found that the pure substance did not yield

a trace of sugar. Various formulæ have been assigned to this substance, viz. Eckert (Jahres. 1864, 608), $C_{28}H_{20}O_{20}$; Oser (Jahres. 1875, 600), $C_{20}H_{20}O_{11}$; Löwe (Zeitsch. anal. Chem. 20, 210), $C_{28}H_{30}O_{15}$; Bötttinger (Ber. 1883, 16, 2712) $C_{15}H_{12}O_9 \cdot 2H_2O$, and Etti (Monatsh. 10, 650), $C_{17}H_{16}O_9$, $C_{18}H_{18}O_9$, and $C_{20}H_{20}O_9$.

Quercitannic acid is described by Etti as a reddish-white powder almost insoluble in water. One of its most characteristic properties is the readiness with which it forms reddish-brown anhydrides when heated by itself or with dilute acids. Thus at 130° – 140° the *first anhydride* $C_{34}H_{30}O_{17}$ is produced, and this by heating with dilute sulphuric or hydrochloric acid gives the *second anhydride* $C_{34}H_{28}O_{16}$. Boiling dilute sulphuric acid again converts the original tannin into the *third anhydride*



These compounds are insoluble in water, but colour a solution of ferric chloride blue (?). Löwe (*l.c.*) again examined an anhydride $C_{28}H_{24}O_{12}$, and an 'oak red' $C_{28}H_{22}O_{11}$. Bötttinger, who prepared the oak red from the tannin by means of dilute sulphuric acid, adopted the formula $(C_{14}H_{10}O_6)_2 \cdot H_2O$. Etti (Ber. 1884, 17, 1823) isolated from the bark of the *Quercus pubescens* (Willd.) a tannin $C_{20}H_{20}O_9$, practically identical with the substance

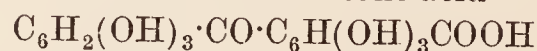


previously found in the *Q. robur* (Linn.), but giving a green solution with ferric chloride, and not a blue, as formerly stated.

When heated with dilute sulphuric acid at 130° – 140° , quercitannic acid gives in addition to anhydride 1.5 p.c. of *gallic acid*, and with strong hydrochloric acid at 150° – 180° the formation of oak red was accompanied by the evolution of methyl chloride (Etti, Monatsh. i. 274). On dry distillation it yields *dimethylcatechol* and *catechol*, and on fusion with alkali *protocatechuic acid*, *catechol*, and *phloroglucinol*.

By the action of bromine on the aqueous bark extract, Bötttinger (Ber. 1883, 16, 2710) obtained *dibromoquercitannic acid* $C_{19}H_{14}Br_2O_{10}$, as a yellow precipitate, and from this *penta-acetyldibromoquercitannic acid* was prepared. Heated with hydrochloric acid at 180° , *methyl chloride* was evolved, and by means of hydroxylamine hydrochloride the compound $C_{19}H_{15}Br_2NO_{10}$ was produced. Reduced with sodium amalgam *hydroquercinic acid* $C_{15}H_{18}O_7$ or $C_{15}H_{16}O_6$ and *hydroquergalic acid* $C_{14}H_{14}O_6$ are formed (Annalen, 263, 121). When suspended in chloroform and further brominated it yields *tetrabromodehydroquercitannic acid*. Quercitannic acid was thus $C_{19}H_{16}O_{10}$, contained five hydroxyls, and the group $COCH_3$.

According to Etti (Monatsh. 10, 647) a further investigation of the tannins $C_{17}H_{16}O_9$ and $C_{20}H_{20}O_9$ has proved that they are not glucosides, but derivatives of a ketone acid



Trimble (The Tannins, 1894, ii. 77) carried out an elaborate investigation of the tannins present in the barks of the *Quercus alba* (Linn.), *Q. coccinea* (Wangenh.), *Q. discolor* (Ait.), *Q. falcata* (Michx.), *Q. palustris* (Du Roi), *Q. prinus* (Linn.), *Q. bicolor* (Willd.), *Q. obtusiloba* (Michx.), *Q. phellos* (Linn.), *Q. rubra* (Linn.), *Q. robur*

(Linn.), *Q. semicarpifolia* (Sm.), employing acetone for the purpose of extraction. The tannins in most cases had a pale yellow colour, gave with ferric chloride a green coloration, and practically identical results with all the usual tannin reagents.

Heated with glycerol at 160°, the tannins of *Q. tinctoria*, *Q. palustris*, *Q. falcata*, and *Q. phellos* yielded catechol, whereas with fused alkali the eight samples examined gave protocatechuic acid. Though all these compounds produce a violet colour on pine wood moistened with hydrochloric acid, phloroglucinol or other phenol was not detected among their decomposition products. Heated with 2 p.c. hydrochloric acid for two and a half hours, a phlobaphene separated, whereas the solution contained protocatechuic acid. Analyses of nine of these tannin preparations showed but little variation, the average being $C=59.79$; $H=5.08$, and approximately correspond with those of Etti (*l.c.*) for the tannin $C_{20}H_{20}O_9$ from *Q. pubescens*, and of Kraemer (Amer. J. Pharm. 1890, 236) for the tannin of *Q. alba*.

According to Feist and Schon (Arch. Pharm. 1920, 258, 317) the tannin of oak-bark contains no methoxyl group and the methoxy compounds associated with it have no tanning properties. No compound is present in the bark from which the tannin might be produced.

Freudenberg and Vollbrecht (Ber. 1922, 55, (B) 2420) have examined the tannin present in the freshly gathered leaves and shoots of the *Q. pedunculata*. This, which was isolated in the crude condition by means of its lead salt, was purified from the associated ellagic acid and quercetin glucosides by means of ethyl acetate and a fractional precipitation of its alcoholic solution with ether. It forms a reddish-yellow amorphous mass, freely soluble in water, alcohol, and acetone, is strongly acidic and gives $[\alpha]_D$ about -35° . As the result of the action of tannase and, under certain conditions, of the *Aspergillus niger*, it is shown that this tannin, which is of a complex character, contains in combination ellagic acid 23–25 p.c., dextrose 5 p.c., and an acid termed by these authors quercussic acid. This is apparently dibasic, and has a molecular weight of about 800. Alkali fusion of quercussic acid yielded no definite products, and the isolation of phloro-glucinol in this manner by others would appear to be due to the contamination of their product with quercetin. According to Freudenberg and Vollbrecht, this tannin is probably a glucoside of quercussic acid, esterified with ellagic acid.

A complex tannin of a similar character has been isolated from the edible chestnut by Freudenberg and Walpriski (Ber. 1921, 54, (B) 1698).

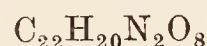
Oak wood tannin, Quercin, Quercic acid, Quercinic acid $C_{15}H_{12}O_9 \cdot 2H_2O$ consists of a light brownish-yellow substance, and is distinguished from the quercitannic acid of oak bark in that its aqueous solution gives a blue, not green, coloration with ferric chloride, and does not yield a precipitate with bromine water (Böttiger, Ber. 1887, 20, 761).

With the object of isolating the tannin in a pure condition, Böttiger acetylated a purified extract of the wood, and decomposed the acetyl compound $C_{15}H_7(C_2H_3O)_5O_9$ by heating it with

water at 135°. By the action of sodium amalgam on the acetyl derivative, Böttiger (Annalen, 263, 110) obtained hydroquercic acid $C_{15}H_{18}O_7$ or $C_{15}H_{16}O_6$, querlactone $C_5H_6O_2$, and an acid which is probably trihydroxybutyric acid.

Hydroquercic acid is a grey-brown, bitter hygroscopic powder, which forms the acetyl derivative $C_{15}H_{14}(C_2H_3O)_2O_6$, the barium salt $(C_{15}H_{15}O_6)_2Ba$, and the lead salt $(C_{15}H_{15}O_6)_2Pb$. Querlactone, on the other hand, forms the salt $(C_5H_7O_3)_2Pb$. As above noted, hydroquercinic acid could also be obtained in a similar manner from quercitannic acid.

Etti (Monatsh. 10, 647) isolated from the wood of the Slavonian oak a tannin $C_{16}H_{14}O_9$ which appeared to be a ketonic compound. This is present in the wood in the form of a readily soluble salt (probably magnesium salt). Crystallised from alcohol, it forms brownish-red microscopic warty spherical masses, insoluble in water, and having the properties of a monobasic acid (*cf.* Fuchs, Monatsh. 9, 1132). With phenylhydrazine it gives the compound



forms a brown amorphous oxime $C_{16}H_{15}NO_9$, and with dilute sulphuric acid at 120°–130° yields gallic acid in addition to a red anhydride. Heated alone at 130°–135°, or in a sealed tube with water at 100°, anhydrides are also produced, which on boiling with hydriodic acid evolve methyl iodide. On long digestion of the tannin $C_{16}H_{14}O_9$ with hydrochloric acid at 100°, a methoxyl group is split off, with production of a yellow coloured acid $C_{15}H_{12}O_9$ in which a methoxyl group is still present. This tannin is therefore probably the dimethyl ether of the ketonic acid formulated above.

On boiling the tannin with dilute sulphuric acid, the anhydride $C_{32}H_{24}O_{16}$ is produced, whilst on heating in a closed tube the anhydrides $C_{32}H_{20}O_{14}$ and $C_{32}H_{18}O_{13}$ were obtained.

The varied results of many of these workers with the oak tannins appear to be due, as suggested by Trimble, to the fact that in many cases they employed oak tannin extracts of doubtful authenticity. Thus it is possible that Etti, who in his earlier work describes the tannin as producing a blue coloration with ferric chloride, was in reality examining oak-wood and not oak-bark preparations, and again the peculiar insoluble property of certain of his tannins, also commented on by Trimble, suggests that in these cases he investigated an anhydride rather than the tannin itself. That oak barks contain a phlobatannin possessing a catechol nucleus appears to be certain from the investigations of Trimble, and it seems probable that in the wood either a pyrogallol tannin or a phlobatannin containing a pyrogallol group is present. Though, as stated above by Etti in the case of the Slavonian oak, this yields phlobaphenes, Stiasny (private communication) considers that such is not usually the property of oak-wood extracts. An interesting point, moreover, apparently not stated in the literature, though well known to tanners, is that oak-wood extracts give some ellagic acid, and on this account impart to leather the 'bloom' so characteristic of this substance.

Oenotannin $C_{19}H_{16}O_{10}$ (?) was obtained by

Gautier from red wine (Bull. Soc. chim. 1877, 27, 496), who describes it as a colourless substance readily soluble in water. It gives a green coloration with ferric chloride solution, by fusion with alkali *protocatechuic acid* and *phloroglucin*, and when exposed to moist air becomes converted into an insoluble red phlobaphene-like substance. According to Heise (Ber. Ref. 22, 823), oenotannin contains gallotannin and is a mixture of three compounds.

Pistachia tannin is present in the leaves of the *Pistacia lentiscus* (Linn.) in addition to some quantity of a gallotannin (Perkin and Wood, Chem. Soc. Trans. 1898, 73, 378), and consists of a pale brown brittle mass which with iron alum solution gives a blue-black coloration. With boiling dilute sulphuric acid a phlobaphene quickly separates, and when fused with alkali, *gallic acid* and *phloroglucinol* are produced.

Phyllæscitannin is the name given by Rochleder to a tannin present in the small leaflets of the horse chestnut, as long as they remain enclosed in the buds (Zeitsch. für Chem. 1867, 84). It is described as an amorphous reddish-brown substance of the formula $C_{26}H_{24}O_{13} \cdot H_2O$, having a strongly astringent taste.

Pinicortannic acid and *cortepinitannic acid* occur in the bark of the Scotch fir, *Pinus sylvestris* (Linn.), and can be separated owing to the fact that in aqueous solution the former only is precipitated by means of lead acetate. Pinicortannic acid forms a reddish-brown powder of the composition $(C_{16}H_{18}O_{11})_2 \cdot H_2O$, which after drying is sparingly soluble in water. It gives a green coloration with ferric chloride, and when boiled with dilute acids gives the phlobaphene $C_{48}H_{50}O_{21}$ (Kawaler, Sitz. Ber. 11, 361).

Pinitannic acid and *oxypinitannic acid* occur in the needles of the Scotch fir, *Pinus sylvestris* (Kawaler), and are distinguished from one another by the fact that the former only is precipitated by lead acetate solution. *Pinitannic acid*, according to Rochleder (Sitz. Ber. 29, 60), also present in the *Thuja occidentalis*, is a reddish-yellow substance which gives a reddish-brown coloration with ferric chloride and when boiled with dilute acids a sparingly soluble red product (phlobaphene).

Oxypinitannic acid, on the other hand, yields a green solution with ferric chloride (Kawaler).

Quebracho tannin or *Quebrachitannic acid*, see QUEBRACHO COLORADO.

Quinotannic acid or *Cinchonatannic acid* obtained from cinchona bark is a light yellow very hygroscopic substance, a solution of which gives a green precipitate with ferric salts. On digestion with boiling dilute sulphuric acid, it is converted into a sugar and cinchona red $C_{28}H_{22}O_{14}$ (Reimbold, Annalen, 143, 270), and from the latter by fusion with alkali, *protocatechuic* and *acetic acids* are produced (Hlasiwetz, *ibid.* 143, 307). According to Schwarz (Sitz. Ber. 7, 250), quinotannic acid has the composition $C_{14}H_{16}O_9$, whereas cinchona red is to be represented as $C_{12}H_{14}O_9$.

Quinovatannic acid, contained in the bark of the *Cinchona nova*, in many respects resembles quinotannic acid (Hlasiwetz, Annalen, 79, 129). With ferric chloride it gives a dark green coloration, and with boiling dilute acids quinoa red

$C_{12}H_{12}O_5$ is produced. On fusion with potash it yields *protocatechuic acid*.

Rhamnotannic acid (so-called), present in buckthorn berries, is in reality not a true tannin.

Rhatany tannin $C_{20}H_{20}O_9$ from the bark of rhatany root *Krameria triandra* (Ruis and Pav.) (Willstein, Jahres. 1854, 656) is described by Raabe (*ibid.* 1880, 1060) as a light yellow powder, readily soluble in water. Its solution gives with ferric chloride a green coloration. When heated with dilute acids it yields rhatany red $C_{22}H_{22}O_{11}$ and a sugar (Grabowski, Annalen, 143, 274), whereas according to Raabe (*l.c.*) no sugar is thus produced and the red substance possesses the composition $C_{20}H_{18}O_8$. By dry distillation rhatany red yields catechol, and *protocatechuic acid* and *phloroglucinol* when fused with alkali.

Rheotannic acid or *Rhubarb tannic acid* $C_{26}H_{26}O_{14}$, derived from rhubarb, forms a yellowish-brown readily soluble powder, the solution of which gives with ferric chloride a black-green precipitate. With boiling dilute acids it gives *rheic acid* (rheumatic acid) $C_{20}H_{16}O_9$ and a fermentable sugar (Kubly, Zeitsch. für Chem. 1868, 308), although according to Tschirch and Neuberger (Schweiz. Wochenschr. Chem. Pharm. 1902, 282) in this manner *rheum-red* $C_{40}H_{32}O_{18}$, *cinnamic acid*, *gallic acid*, and sugar are produced. According to Gilson (Chem. Zentr. 1903, i. 722, 882), two glucosides are present, *glucogallin* $C_{13}H_{16}O_{10}$, giving gallic acid and dextrose, and *tetrarin* $C_{32}H_{32}O_{10}$, from which *rheosurin* $C_{10}H_{12}O_2$, *cinnamic acid*, and *gallic acid* can be produced. According to Krembs (Inaugural Diss. 1903, Berne), a catechin is also present in rhubarb.

Rhodotannic acid $4C_{14}H_{12}O_7 \cdot 3H_2O$, found in the leaves of *Rhododendron ferrugineum* (Linn.), is an amber-coloured substance which gives a green coloration with ferric chloride solution. Heated with dilute mineral acids, a reddish-yellow precipitate of *Rhodoxanthin* $C_{14}H_{14}O_8$ is produced (Schwarz, Sitz. Ber. 9, 298).

Rostra bark (*R. fotsy* and *R. meno*) is obtained from trees belonging to the genus *Eugenia Myrtaceæ*. It is thick and fibrous, is easily extracted, and contains moisture 13.75 p.c., soluble tans 12.62 p.c., soluble non-tans 12.17 p.c., insoluble matter 61.46 p.c. The tannin (mixed pyrogallol and catechol tannins) produces a very soft, dark reddish-brown leather. Lalona (*Weinmannia bojeriana*) bark is a thinner bark which is not so easily extracted, and contains moisture 11.25 p.c., soluble tans 13.75 p.c., soluble non-tans 2.68 p.c., and insoluble matter 72.32 p.c. The tannin is a mixture of pyrogallol and catechol tannins, and produces a fairly soft leather, which is not very dark coloured. Filao bark (*Casuarina equisetifolia*) contains a catechol tannin which is easily extracted, and produces a light-coloured leather. The bark contains moisture 10 p.c., soluble tans 15.31 p.c., soluble non-tans 3.65 p.c., insoluble matter 71.04 p.c. Badamier bark (*Iterminalia Catappu*), also known as Hatafa, is a thin bark, easily extracted, contains a pyrogallol tannin, and yields a fairly soft light-coloured leather. It contains moisture 10.6 p.c., soluble tans 11.81 p.c., soluble non-tans 4.44 p.c., insoluble matter 73.15 p.c. (Heim and Cercelet, J. Soc. Leather Trades

Chem. 1923, 7, 361-365; J. Soc. Chem. Ind. 42, 1923, 1083 A).

Rubinic acid, v. CATECHU.

Rubitanic acid $2C_{14}H_{22}O_{12} + H_2O$ was obtained by Willigk (Annalen, 82, 340) from the leaves of *Rubia tinctorium* (Linn.). It gives a green colour reaction with ferric chloride.

Sequiatannic acid $C_{21}H_{20}O_{10}$ was isolated from the cones of *Sequoia gigantea* (Torr) (California) by Heyl (Pharm. Zentr. 1901, 42, 379) as a reddish-brown powder, soluble in water and yielding the salts $MgC_{21}H_{18}O_{10}$ and $CaC_{21}H_{18}O_{10}$. Boiled with dilute sulphuric acid, a phlobaphene, *gallic acid*, and a sugar are produced. The *hexa-acetyl* $C_{21}H_{14}O_{10}(C_2H_3O)_6$, *hexabenzoyl* $C_{21}H_{14}O_{10}(C_7H_5O)_6$, and *bromine* $C_{21}H_{15}O_{10}Br_5$, derivatives of this tannin are amorphous.

Sorbitannic acid, from the juice of the ripe berries of the mountain ash, *Sorbus aucuparia* (Linn.), forms a thick syrupy mass, which gives a green coloration with ferric chloride solution. It yields *catechol* on dry distillation, and *protocatechuic acid* and *phloroglucinol* when fused with alkali (Vincent and Delachanal, Bull. Soc. chim. [ii.] 47, 492).

Spruce-bark tannin, $C_{21}H_{20}O_{10}$ (?) gives, according to Böttinger, an unstable bromo derivative $C_{21}H_{14}Br_6O_{10}$. This reacts with hydroxylamine hydrochloride, and with hydrochloric acid at 180° - 190° evolves *methyl chloride*. The *penta-acetylpentabromo* derivative



is known. With boiling dilute hydrochloric acid the tannin yields *spruce red* which gives the acetyl derivative $C_{42}H_{27}(C_2H_3O)_7O_{17}$, and when suspended in chloroform and treated with bromine the compound $C_{42}H_{24}Br_{10}O_{17}$ (Böttinger, Ber. 17, 1127).

Strawberry-root contains a tannin *fragarianin* (Phipson, Jahres. 1878, 891), the solution of which gives a green colour with ferric chloride. Boiling dilute hydrochloric acid forms *glucose* and a red substance *fragiarin*. On dry distillation the tannin gives traces of *catechol*, and when fused with alkali *protocatechuic acid* is produced.

Tannecortepinic acid $C_{28}H_{26}O_{12}$, according to Rochleder and Kawalier (Sitz. Ber. 29, 23), can be isolated from the bark of young Scotch firs collected in the spring time. Ferric chloride gives a green coloration and boiling dilute acid a phlobaphene in addition to a little sugar.

Tannopinic acid $C_{28}H_{30}O_{13}$ (?) is sometimes present in the needles of the Scotch fir gathered in the spring (Rochleder and Kawalier). In the winter time, oxypinitannic acid (*l.c.*) appears to take its place.

Tea tannin is probably identical with the quercitannic acid of oak bark (Stenhouse, Phil. Mag. 23, 332; Rochleder, Annalen, 63, 205; and Hlasiwetz and Malin, J. pr. Chem. [i.] 101, 109).

Tormentilla tannin $C_{26}H_{22}O_{11}$, from the root of *Potentilla tormentilla* (Neck.), is an amorphous reddish powder, which colours ferric chloride solution blue-green. Boiled with dilute acids it produces *tormentil-red* without appreciable formation of sugar, and this appears to have the same composition as the tannin itself. With fused alkali *phloroglucinol* and *protocatechuic acid* are obtained. The root also contains a substance

which yields *ellagic acid* when boiled with potash solution (Rembold, Annalen, 145, 5).

Viridic acid $C_{14}H_{20}O_{11}$ (?), which exists in coffee beans as a calcium salt (Rochleder, Annalen, 63, 197), is obtained by the air oxidation of an ammoniacal solution of caffetannic acid, and forms a brown amorphous mass, the alkaline solutions of which are green. The salts $Ba_2C_{14}H_{16}O_{11}$, $PbC_{14}H_{12}O_8$, and $PbC_{14}H_{14}O_9$ have been described (*cf.* also Vlaanderen and Mulder, Jahres. 1858, 261).

Willow bark tannin.—The bark of *Salix triandra* (Linn.) contains a glucoside tannin which gives a green colour reaction with ferric chloride, and when boiled with dilute sulphuric acid a brown-red precipitate (Stenhouse, Proc. Roy. Soc. 11, 403; Johanson, Arch. Pharm. [iii.] 13, 103).

Tannins are frequently accompanied in the plant by yellow colouring matters, and it has been pointed out by Perkin that a relationship is usually to be observed between these compounds in respect of the phenolic nuclei present in each. Thus catechu contains catechutannic acid and quercetin, both of which contain phloroglucinol and catechol groups, whereas both the cyanomacclurin and morin of Jakwood (*Artocarpus intergrifolia*, Linn.) yield phloroglucinol and β -resorcylic acid. Again, in sumach (*R. coriaria*, Linn.), *Pistacia lentiscus*, Linn. (leaves) and *Hæmatoxylon campeachianum*, Linn. (leaves), a gallotannin and myricetin exist, both of which are pyrogallol derivatives.

Other similar instances of this relationship could be cited; and where a divergence of this rule at first sight seems evident, this is frequently more apparent than real, as in the case of Young Fustic (*R. cotinus*, Linn.), which is known to contain a gallotannin and fisetin (catechol and phloroglucinol). From the reactions of the wood extract, however, a catechol tannin must also be present.

GALL-NUTS.

These are morbid excrescences produced by the puncture of an insect called *Cynips gallæ-tinctoriæ* upon the leaves and young twigs of certain kinds of oak trees, more especially those of *Quercus infectoria* (Oliver), *Q. lusitanica* (Lam.), growing in the East Indies, Persia, and the Levant. If the fully developed nut be broken open it will be seen to contain a central cavity, in which the larva of the insect will be found. As a rule the galls are collected before the larvæ are fully developed, and therefore before they have perforated the galls and escaped as mature insects. In this condition they contain the most tannic acid and are known as *blue*, *black*, or *true nuts*. The less valuable or perforated variety are larger and paler in colour and are known as *white* or *false nuts*.

Aleppo galls are one of the best varieties on the market, and should contain from 50-60 p.c. of tannic acid. This same oak, the *Quercus infectoria*, also bears a large gall known as the Apple of Sodom, due to a different insect, which contains from 24 to 34 p.c. of tannin and has been used for tanning purposes.

Other varieties are Smyrna galls, Austrian, and Hungarian galls, and of these the first named are considered the best. English oaks

yield several species of galls and oak apples, which, however, are not of much value.

Chinese galls afford the richest known source of tannin, containing from 57 to 60 p.c. These galls are produced by the punctures of an aphid, *Schlechtendaria sinensis*, on the leaf stalks of *Rhus javanica*, L., and possibly some nearly allied species in China, but they are not found on *R. coriaria*, as stated by several authors. The galls are hollow and possess very thin walls, but are much larger and more irregular in shape than the ordinary Aleppo variety; moreover, when freshly gathered, they are covered with a very fine down. They are much esteemed owing to their richness in tannin matter. On this account they are largely employed for the manufacture of *tannic acid*. At present Chinese galls are derived solely from China and Japan. From the investigations of C. Sasaki on the insect, its life-history is well known, and it should be possible to breed it in French Indo-China if the plant host *Rhus javanica* were cultivated for it to live on (A. Chevalier, *L'Union pharm.* 1923, 64, 327; *Pharm. J.* 1924, 112, 56).

Gall-nut extract is employed for mordanting purposes when very delicate shades are required. In addition to tannic acid, all varieties of gall-nuts appear to contain minute traces of ellagitanic acid.

CHESTNUT EXTRACT.

The wood of the Spanish chestnut, *Castanea vesca*, though it contains only 3–6 p.c. of tannin, is the source of the much-valued chestnut extract. The bark contains more tannin than the wood (17 p.c.), but is not much used. The tree, which grows to from 60 to 80 feet in height, is abundant in Italy, the South of France, and Corsica, where it forms extensive forests, and it is also very common in America.

Trimble (The Tannins), who very carefully examined the tannin, obtained analytical data and reactions which indicated that it was identical, or nearly so, with gallotannin, but it is probable that this wood also contains traces of a phlobatannin, for a certain quantity of a red colouring matter is also present, which resembles in character a phlobaphene. Some writers have suggested that chestnut tannin is a methyl ether of ordinary gallotannin, but there is apparently no definite evidence in support of this assumption.

Chestnut is employed almost entirely in the form of extract, the strength of which varies, but usually contains from 26 to 32 p.c. of tannin. The extract is frequently decolorised, and sometimes mixed with quebracho extract and other materials. Chestnut tannin is the tannin which is most largely employed for the dyeing of silk. *Castanea vesca* appears to be frequently confused with the horse-chestnut, *Æsculus hippocastanum*. The tannin derived from this latter is, however, of little or no practical value.

SUMACH.

True sumach consists of the dried and usually powdered leaves of the genus *Rhus* (order *Terebinthaceæ*), and is useful for tanning the finer kinds of leather, and also in dyeing and calico

printing on account of the tannin matter present in it.

Sicilian sumach, the variety most esteemed in this country and throughout Europe, consists of the leaves of the *Rhus coriaria* (Linn.), a shrubby bush cultivated to a large extent in Sicily, where the sumach industry is of considerable importance. When the plant is about to flower the younger twigs are removed, dried in the sun, and subsequently beaten to remove the leaves and flower panicles. The sumach is imported sometimes in leaves, but more often in the form of powder, and should contain about 25 p.c. of tannin, although as much as from 27 to 32 p.c. may occasionally be found.

According to Löwe (*Zeitsch. anal. Chem.* 12, 128), the tannin matter present, $C_{14}H_{10}O_8$, is ordinary gallotannin; indeed it is well known that when an aqueous extract of the sumach is boiled with dilute sulphuric acid, considerable quantities of gallic acid are produced. On the other hand, Strauss and Geschwender (*Zeitsch. angew. Chem.* 1906, 1121), who isolated the tannin according to Löwe's instructions, detected the presence of a methoxy group, and suggest the formula $C_{32}H_{29}O_{11} \cdot OMe$.

Sicilian sumach contains also a trace of an ellagitannin and myricetin $C_{15}H_{10}O_8$ to the extent of about 0.1173 p.c. (Perkin and Allen, *Chem. Soc. Trans.* 1896, 69, 1299), the latter colouring matter having been previously mistaken by Löwe (*Zeitsch. anal. Chem.* 1874, 12, 127) for quercetin.

Considerable quantities of sand and sometimes particles of magnetic iron ore, which cause black stains, are often to be found in sumach (Procter, *Principles of Leather Manufacture*, 1903, 271) (*cf.* also Trotman, *J. Soc. Chem. Ind.* 1904); and it is frequently highly adulterated in the ground condition with the leaves and twigs of various plants. Of these, the *Pistacia lentiscus* (Linn.) ('schinia' or 'skeñs'), *Coriaria myrtifolia* (Linn.), (French sumach or 'stinco'), *Tamarix africana* (Poir.) (brusca), *Tamarix gallica* (Linn.), *Ailanthus glandulosa* (Desf.), *Ficus carica* (Linn.), *Vitis vinifera* (Linn.), other species of the *Rhus* family and also the ground branches ('gambuzza,' 'gammuzza') of the *Rhus coriaria* itself, are known to be employed. These sumach adulterants also contain tannin matters, but for tanning and dyeing purposes are as a rule much inferior to sumach itself.

The *Pistacia lentiscus* (Linn.) (mastic tree), a small tree about 20 feet high with evergreen leaves, grows abundantly in Cyprus. The leaves of this plant constitute the most important sumach adulterant, and about 10,000 tons are said to be exported from Tunis to Sicily annually and re-exported thence (as sumach?). According to Procter (*l.c.*) the leaves contain 12–19 p.c. of a catechol tannin. A good plump leather can be obtained from this material, but of a faintly reddish tint, the result being intermediate in character between those which are given by oak bark and sumach. Its presence in sumach is to be deprecated, and in many cases leads to injurious results. A considerable quantity, however, is consumed at Lyons in France as an assistant dyeing material for silk stuffs.

According to Perkin and Wood (*Chem. Soc.*

Trans. 1898, 73, 374), these leaves contain a tannin closely allied to, if not identical with, ordinary gallotannic acid, as when an aqueous extract is boiled with dilute sulphuric acid a considerable quantity of gallic acid is produced. A second tannin or tannin glucoside is also present which, although possessing the general characteristics of the so-called 'catechol' tannins in that it yields a red phlobaphene, and as noted by Procter, a reddish-coloured leather, gives, by fusion with alkali, gallic acid and phloroglucinol.

In addition to these tannins, myricetin (probably as glucoside) $C_{15}H_{10}O_8$ is also present to the extent of about 0.15 p.c.

Tamarix africana (Poir.) is a small shrub or tree characterised by its twiggy branches and minute scale-like leaves. The small twigs are collected in Tunis and imported into Sicily for the adulteration of sumach (Procter).

According to Perkin and Wood (*l.c.*) the leaves contain a tannin probably identical with gallotannin in addition to a small quantity of an ellagi-tannin. A trace of yellow colouring matter is also present and consists of a quercetin methylether $C_{16}H_{12}O_7$.

The *Tamarix gallica* (Linn.) closely resembles in appearance the *Tamarix africana* and flourishes in Cyprus, where the latter is not found. According to Procter, it contains 8.4 p.c. of tannin matter.

Ailanthus glandulosa (Desf.) is a tree of large size and handsome appearance, native of India and China, but common on the Continent. The leaves contain 11.2 p.c. of tannin matter (Procter), and this resembles gallotannin, although a trace of an ellagitannin is also present (Perkin and Wood). Curiously enough, although it contains so high a percentage of tannin, leather is scarcely tanned by an extract of these leaves, but is merely stained a dull dirty colour. This material is therefore of little use for tanning purposes, and as an adulterant of sumach exerts a deleterious influence. A small quantity of quercetin can be isolated from the leaves.

The leaves of the *Ficus caria* (Linn.) (common fig tree) contain 1.6 p.c. of tannin (Procter) and a trace of a yellow colouring matter (Perkin and Wood). Skin is untanned by an extract of these leaves, but acquires, during the process, a dirty olive tint.

Gambuzza consists of the small stalks branching from the main root of the *Rhus coriaria* (Linn.), which are ground to powder and mixed with sumach. The material contains some quantity of a tannin resembling gallotannin, together with a trace of myricetin.

Attempts to detect the presence of these adulterants in sumach by chemical methods have not given satisfactory results, but should a prolonged boiling of the extract with dilute sulphuric acid cause the gradual precipitation of phlobaphene, the presence of the leaves of the *Pistacia lentiscus* may be suspected.

Microscopical examination is preferable, and an elaborate work on this subject has been carried out by Andreasch (Sicilianischer Sumach und seine Verfälschung, Wien, 1898); the book, however, is unsuitable for abstraction. A useful method, now generally adopted by leather trades chemists, has been devised by Lamb and

Harrison (J. Soc. Dyers, 1899, 14, 60), and is based upon the behaviour of the leaf mixture with warm nitric acid. Under such treatment, the more delicate leaf structure of sumach itself is completely destroyed, whereas the strong cuticles of *Pistacia lentiscus*, *Coriaria myrtifolia*, *Tamarix africana*, and *Ailanthus glandulosa* are unaffected and can then be readily recognised (*cf.* also Lamb. *ibid.* 1904, 20, 265). Again, the leaves of the *R. coriaria* are very easily distinguished from those of other plants employed for their adulteration, in that both upper and lower cuticles are covered with a dense growth of hairs (Priestman, J. Soc. Chem. Ind. 1905, 24, 231).

Venetian sumach or *Turkish sumach* consists of the leaves of the *Rhus cotinus* (Linn.), a small tree, the wood of which constitutes the yellow dyestuff known as 'Young Fustic.' The material contains about 17 p.c. of tannin, which resembles ordinary gallotannin, together with a trace of an ellagitannin. The presence of myricetin $C_{15}H_4O_2(OH)_6$ in these leaves is interesting, in view of the fact that in the wood itself fisetin $C_{15}H_6O_2(OH)_4$ is present (Perkin, Chem. Soc. Trans. 1898, 73, 1016).

American sumach.—The leaves of numerous varieties of *Rhus* are employed in the United States for tanning and dyeing purposes, and of these the *R. glabra* (Linn.) very largely takes the place of Sicilian sumach. It contains about 25 p.c. of a tannin closely resembling gallotannin, but produces a leather of very much darker colour than the Sicilian product.

Of the other varieties, *R. typhina* (Linn.) or 'Virginian sumach' (10–18 p.c.), *R. cotinoides* (Nutt.) (21 p.c.), *R. semialata* (Murr.) (5 p.c.), *R. aromatica* (Ait.) (13 p.c.) (Procter), *R. metopium* (Linn.) (about 8.2 p.c. of tannin, probably gallotannin, together with traces of both quercetin and myricetin) (Perkin, Chem. Soc. Trans. 1900, 77, 427), *R. copallina* (Linn.), *R. pumila* (Michx.), and *R. toxicodendron* (Linn.), are to be found in the States. Among these, *R. glabra* and *R. copallina* are considered to be worthy of extended cultivation.

In India, numerous species of the genus *Rhus* are known to exist (Watt's Dictionary, 'Economic Products of India'), and again in Algeria the *R. pentaphylla* (Desf.) is used by the Arabs for tanning goat-skins. Finally, the *Anaphrenium argenteum* (E. Mey), (*R. thunbergii*) (Cape of Good Hope), 28 p.c. of tannin (bark), probably of the catechol class (Procter), and the *Rhodosphaera rhodanthema* (Engl.) (*Rhus rhodanthema*) (New South Wales), 9.5 p.c. of tannin (leaves), resembling gallotannin, are worthy of mention. The latter plant, also known as the 'yellow cedar,' closely resembles the *R. cotinus*, and it is interesting to note that although the wood of this tree contains fisetin $C_{15}H_4O_2(OH)_4$, the colouring matter of the leaves is quercetin $C_{15}H_5O_2(OH)_5$ (Perkin, Chem. Soc. Trans. 1898, 73, 1017).

French sumach is derived from the *Coriaria myrtifolia* (Linn.), a low deciduous shrub, native of Southern Europe, and has been referred to above as an adulterant of Sicilian sumach. In addition to tannin (15.6 p.c., Procter), which consists probably of ordinary gallotannin together with a little ellagitannin, it contains the poisonous glucoside *coriamyrtin* (Riban,

Chem. Zeit. 1867, 663) and a trace of quercetin (Perkin, Chem. Soc. Trans. 1900, 77, 428). According to Procter, the colour of leather tanned by these leaves is very satisfactory and practically equal to that produced by genuine sumach (*R. coriaria*). It is also employed in black dyeing.

Cape sumach consists of the leaves of the *Colpoon compressum* (Berg.) (*Osyris compressa*, *Fusanus compressus*, *Thesium colpoon*), and is much used in South Africa under the name of 'Pruimbast.' The bush is found in the mountains, where it grows to the height of about 6 feet, and only the younger leaves are gathered. These leaves contain about 23 p.c. of tannin (Procter), which has been isolated as a hygroscopic transparent glassy mass and is probably a phlobatannin glucoside. With boiling dilute acid, a reddish-brown phlobaphene gradually separates, and on fusion with alkali protocatechuic acid is produced (Perkin, Chem. Soc. Trans. 1897, 71, 1135). In addition to tannin there is also present a considerable quantity of the quercetin glucoside *Rutin* (*Osyritrin*) (Chem. Soc. Trans. 1910, 98, 1776). According to Procter, this material forms a useful substitute for Sicilian sumach.

In lieu of the *Colpoon compressum*, a tanning agent known as 'broach leaves' (botanical origin lacking) appears to be considerably employed in South Africa. It contains about 19.9 p.c. of tannin of the so-called 'catechol' variety, together with traces of both quercetin and myricetin (Chem. Soc. Trans. 1898, 73, 384).

Russian sumach consists of the leaves of the *Arctostaphylos uva ursi* (Spreng.) (Bearberry), and is said to contain about 14 p.c. of tannin, which, according to Perkin (Chem. Soc. Trans. 1900, 77, 424), consists of a gallotannin together with traces of an ellagitannin. Minute amounts of both quercetin and myricetin have been isolated from this material.

Considerable quantities of 'sumach extract' are now manufactured for dyeing and tanning purposes from genuine Sicilian sumach, and this is usually found on the market as a brown treacly liquid of about 52°Tw. So-called *decolorised* extracts are also prepared to compete with ordinary tannic acid, and for this purpose the addition of blood albumen to the dilute extract at about 48°, then raising the temperature to 70°, and subsequently filter-pressing, gives the most satisfactory results. Sulphurous acid again is employed to brighten the colour of extracts, and acts partly as a weak acid in decomposing the inorganic salts of the tannin or colouring matter and partly as a reducing agent. In this case it is usual to pass sulphur dioxide through the liquor before concentration (Procter).

Badan root a Siberian tanning material.—Badan (*Saxifraga crassifolia*, or *Bergenia crassifolia*, Engl.) is a plant with large thick leaves and a peculiarly shaped branched root, about 25 mm. thick. When freshly broken the root is rose-red in colour. It dries very hard. The plant grows best in hilly parts, and the tannin content of the root (air dried) increases from 15.1 p.c. at a height of 450 m. to 22.5 p.c. at a height of 2300 m. The composition of a sample of the root was as follows: Moisture, 6.3 p.c. ;

tans, 17.16 p.c. ; non-tans, 23.64 p.c. ; insoluble tans, 1.00 p.c. It tans leather a bright yellow or orange-red colour. It can be used for tanning sole leather, but it is more suitable for upper leather. About 115,000 tons of dried roots are available annually. The product is easily leached and a sulphited extract has been prepared containing tans, 35.00 p.c. ; non-tans, 47.0 p.c. ; and insoluble matter, 2.44 p.c. (Smetkin, Collegium, 1924, 255 ; J. Soc. Chem. Ind. 1924, 43, B. 758).

MYROBALANS.

This very important tanning material consists of the fruit or nuts of the *Terminalia chebula*, a tree of from 40 to 50 ft. high, which grows in China and the East Indies. These nuts, which resemble a somewhat shrivelled plum, contain from 30 to 40 p.c. of tannin, the unripe fruit containing the largest amount. They should be bright in colour, and not soft, and require to be kept in a dry place, otherwise they absorb moisture and are then difficult to grind. The tannin present consists of a gallo-tannin, which is at least in part chebulinic acid, together with a fairly large amount of ellagitannin, and this, owing to fermentation and other causes, is decomposed to some extent during lixiviation into ellagic acid. Myrobalans from the dyer's point of view is one of the most serviceable tannin materials at the present time. Large quantities of its extract, especially as purified or decolorised extracts, are manufactured, and these are employed for cotton dyeing, in the black dyeing of silk, and in tanning.

VALONIA.

Valonia (*Valonée*, Fr. ; *Valonea*, *Ackerdoppen*, *Orientalische Knopperrn* (Ger.)), an important tanning material, is the acorn cup of certain species of oak, usually *Quercus aegilops* (Linn.), and probably *Q. macrolepis*, *Q. graeca*, *Q. ungeri*, and *Q. coccifera* (Linn.). The former is most prolific in the highlands of Morea, Roumelia, Greek Archipelago, Asia Minor, and Palestine, whereas the *Q. macrolepis* forms great forests in Greece. These acorn cups have a diameter up to about 1½ inches, and in good condition possess a bright colour.

The fruit ripens in Asia Minor about July or August, and the trees are then shaken, and the material left on the ground to dry ; this is subsequently collected into heaps, and allowed to ferment for some weeks, until the acorn contracts and falls from the cup. The acorn, which contains but little tannin, is employed for feeding purposes.

In Greece distinct qualities of valonia are known, the best (*chamada*) collected about April before the fruit is ripe, a second (*rhabdisto*) in September or October, and a third little-used inferior variety (*charcala*).

Smyrna valonia may contain 40 p.c., Greek 19–30, and Candia valonia 41 p.c. of tannin matter, which consists of a mixture of a gallo-tannin and an ellagitannin. Valonia is, indeed, an excellent source for the preparation of ellagic acid, because it so readily yields a product easy to purify. Extract of valonia frequently undergoes fermentation with decomposition of ellagic

acid, and to avoid this the employment of antiseptics is to be recommended.

Valonia is especially suited for the manufacture of sole leather, and together with gambier and other materials for dressing leather, but is little employed for dyeing purposes (cf. Procter, *Principles of Leather Manufacture*, 259).

DIVI-DIVI.

Divi-divi consists of the dried pods of the *Caesalpinia coriaria* (Willd.), a tree 20–30 feet high, found in the West Indies and Central America. The pods are about 3 inches long and $\frac{3}{4}$ inch broad, are very thin, and frequently resemble in shape the letter S. From 40 to 45 p.c. of tannin is present, which consists of ellagitannin and probably also a gallotannin. Extracts of this material have a somewhat unfortunate tendency to ferment, with simultaneous development of a deep-red colouring matter; but this can be prevented to some extent by the use of antiseptics. Divi-divi is largely imported for the preparation of leather, and is also employed for black dyeing, but its use is far more limited in this latter respect than myrobalans.

ALGAROBILLA.

Algarobilla consists of the pods of the *Caesalpinia brevifolia* of Chile. The tannin appears to consist principally of ellagitannin, and this lies in resinous particles loosely attached to the somewhat open framework of the fibre. It is one of the strongest tannin matters known, and contains on the average 45 p.c. In character it resembles divi-divi, its extract being somewhat liable to fermentation. It is very suitable for tanning and also for dyeing purposes.

QUEBRACHO COLORADO.

The *Quebracho colorado* are anacardinaceous trees belonging to the genus *Quebrachia*, growing in the northern part of the Argentine Republic, the wood of which constitutes the well-known tannin substance 'quebracho.' It is imported into this country in the form of logs and is employed for tanning, either in the chipped condition or in the form of extract. Their wood is extremely hard, as the name 'quebracho' (axe-breaker) denotes, and its specific gravity varies from 1.27 to 1.38.

Jean (Bull. Soc. chim. 1880, 33, 6) found that it contained 15.7 p.c. of a tannic acid, not identical with that of oak bark or chestnut wood, whereas Procter (*Leather Manufacture*, 1903, 269) estimates it to contain about 20 p.c. of a tannin yielding reds (phlobaphene), and containing catechol and phloroglucinol nuclei. This tannin is somewhat sparingly soluble in water and can only be used in weak liquors, but gives a firm reddish leather.

In order to isolate the tannin, Strauss and Geschwender (Zeitsch. angew. Chem. 1906, 19, 1121) extract the bark first with chloroform and then with alcohol. Addition of water to the alcoholic extract causes the separation of phlobaphenes, and from the clear liquid concentrated in a vacuum the tannin is precipitated by lead acetate, the lead salt being collected, suspended in water and decomposed with sulphuretted hydrogen. The resulting solution

is evaporated to dryness, the residue dissolved in alcohol and poured into ether. Thus obtained it consists of a light flaky mass, which is hygroscopic and becomes sticky on exposure to moist air.

According to Arata (Jean, Bull. Soc. chim. 1879, 306) *quebracho tannin* $C_{26}H_{24}O_{10}$ gives *catechol* on dry distillation, with nitric acid *oxalic* and *picric acids*, by fusion with alkali *phloroglucinol* and *protocatechuic acid*, whereas, by the latter method, Nierenstein isolated also *hydroquinone* and *resorcinol* (Collegium, 1905, 65). According to the latter author, the *quebracho colorado* probably contains three tannins. By treating a cold aqueous extract of the *quebracho colorado* with bromine, Böttinger (Ber. 17, 1123) obtained a reddish-yellow compound containing 42.1–44.5 p.c. of bromine. Nierenstein, who isolated the tannin according to Trimble's method (The Tannins), treated the solution with lead acetate, filtered, and on adding bromine to the clear liquid obtained a precipitate of *monobromoquebrachotannin* $C_{16}H_{14}BrO_8$, which consists of a cinnabar red powder, and on digestion with alcoholic potash gives *isovanillic acid* and *monobromoquebrachylic acid* needles, m.p. 119°–120°.

Strauss and Geschwender (l.c.) consider that *quebracho tannin* is identical with *malettotannin*, and with the tannin from cinchona bark, and ascribe to it the formula $[C_{41}H_{44}O_{18}(OMe)_2]_2$. With a mixture of acetic anhydride and acetic acid an *acetyl* compound $(C_{30}H_{22}O_{11}Ac_6)_2$, colourless powder, is produced, and a corresponding *benzoyl* derivative $(C_{30}H_{22}O_{11}Bz_6)_2$ can also be prepared.

Quebracho phlobaphene, on distillation with zinc-dust, yields anthracene (Nierenstein, Ber. 1907, 40, 4575).

According to Arnaudon the wood contains a colouring matter which gives a fine yellow dye, and this has been examined by Perkin and Gunnell (Chem. Soc. Trans. 1896, 69, 1304), and found to be identical with *fisetin*, the colouring matter of young fustic. This compound, which appears to exist in the wood as glucoside, gives on fusion with alkali *protocatechuic acid* and *resorcinol*, and may account for the appearance of the latter phenol among the hydrolytic products of the crude tannin itself. According to Perkin and Gunnell, when an extract of the *quebracho colorado* is digested with boiling dilute acid a small quantity of *ellagic acid* is obtained.

In addition to the tannins above described, the *quebracho colorado* is the source of the so-called "quebracho resin," which collects as a thickened juice in the crevices of the tree. It has been examined by Arata (Chem. Soc. Abstr. 1878, 984), who states that it is easily soluble in alcohol or ethyl acetate, insoluble in benzene. By fusion with alkali it gives *protocatechuic acid* (?) and *phloroglucin*, and by the action of nitric acid, oxalic and picric acids are produced.

A considerable amount of the tannin contained by the *quebracho colorado* is of a sparingly soluble nature, and is deposited to some extent from a hot aqueous extract on cooling. This product may be rendered soluble by treatment with alkalis or alkaline sulphites, and a large quantity of the so-called 'soluble' *quebracho* extracts are prepared by heating the material in closed vessels with bisulphites, sulphites,

sulphides, or even caustic alkalis (Lepetit, Dollfus and Gansser, Eng. Pat. 1896, 8582; cf. Procter, Leather Manufacture, 338). A. G. P.

TANNINS, SYNTHETIC. (Artificial tannins: *Syntans*.) A synthetic tan is made by treating a carbohydrate with sulphuric acid so as to produce a solution of hexose in sulphuric acid, and adding to such solution a quantity of phenol less than that necessary to combine with the acid and hexose to form a phenolsulphonylhexose, the sulphonating conditions being maintained until a substantial quantity of penta-*p*-phenolsulphonylhexose is formed (S. Kohn, Assn. to Rohm and Haas Co. U.S. P.). Free acids present in vegetable, mineral, or synthetic tanning agents, or sulphonic groups contained in synthetic tanning agents, such as sulphonated phenol-formaldehyde or other condensation products, are neutralised by the addition of ammonia or a neutral ammonium salt, or an organic base—suitable bases include pyridine and quinoline, or crude mixtures of these, aniline, naphthylamine, and other simple primary, secondary, or tertiary bases of the aliphatic, heterocyclic, or aromatic series; hydrolytic decomposition products of proteins, such as those produced from leather itself, with or without the use of catalysts, enzymes, and ferments; and glyccoll, or the hydrolytic decomposition products of gelatin (W. Moeller, Eng. Pat. 200262, 1922; J. Soc. Chem. Ind. 1923 (see LEATHER, vol. iv. p. 98).

TANNINTHYMOLMETHANE. A condensation product of tannin, formaldehyde and thymol.

TANNISMUT, TANNOFORM, TANNOPIN, TANNOSAL, TANNOGUAIAFORM, TANNO-CRESOFORM, TANNIGEN, TANNALBIN, TANARGAN, TANNOCASUM, TANNOETHY-MAL, TANNYL, TANOCOL *v.* SYNTHETIC DRUGS.

TANNOBROMINE. Trade name for a combination of dibromotannin and formaldehyde.

TANTALITE. A heavy, black mineral consisting essentially of iron tantalate FeTa_2O_6 , and crystallising in the orthorhombic system. The ferrous iron is usually in part, or sometimes almost wholly, replaced by manganous oxide, forming a passage to the variety known as *manganotantalite*. In the same way, tantalic acid is replaced isomorphously by columbic acid, forming a gradual passage into the species columbite (*q.v.*). The general formula for this isomorphous group is thus $(\text{Fe}, \text{Mn})(\text{Ta}, \text{Cb})_2\text{O}_6$. With the variation in the relative amounts of columbic and tantalic acids the sp.gr. ranges from 5.3 (columbite) to about 7.8 for nearly pure tantalite. In their other physical and crystallographic characters the two species are, however, remarkably similar. They are iron-black to brownish-black with a sub-metallic lustre, and a dark brown to black streak; $H.=6$. They are usually found as crystalline grains, or forming large rough masses by the sub-parallel grouping of prismatic crystals; well-formed crystals with brilliant faces are occasionally met with. They occur embedded in granitic rocks, more especially in pegmatite-veins intersecting these rocks: a common associated mineral is cassiterite. The columbium-rich members are of much more frequent occurrence than those at the tantalum end of the series.

Tantalite has long (since 1802) been known from several localities in Finland, and it has also

been found in a few other countries. The greatly increased demand for tantalum since its introduction in the metallic filament of electric lamps in 1904 has led to the discovery of several new localities, more particularly in Australia; and it is this continent that now supplies most of the raw material. It has been obtained in commercial quantities at Wodgina in the Pilbara gold-field, and at Greenbushes in the Blackwood Ranges, in Western Australia; and on the Finnis river near Port Darwin in Northern Territory. At Wodgina it occurs in pegmatite-veins, composed of quartz, felspar (mainly albite), mica (muscovite and lepidolite) and tantalite, the last-named in crystalline masses from the size of a shot to those weighing 5 cwt. The tantalite is collected from the surface soil, from the neighbouring alluvial deposits, and by quarrying the pegmatite. At Greenbushes it is found as grains and irregular lumps, reaching 13 lbs. in weight, in the alluvial deposits of tin-stone. On the Finnis river the mineral occurs with cassiterite scattered through a large intrusion of greisen. In the Ndanga district, Victoria tin-field, Southern Rhodesia, tantalite (sp.gr. 7.06–7.30) as lumps up to 3 lbs. in weight has been found in some abundance together with cassiterite in rubble overlying pegmatite and greisen. The mineral is also recorded from other districts in Rhodesia (A. E. V. Zealley, Proc. Rhodesia Sci. Assoc. 1917, 16, 21).

Analyses: I, Tantalite ('skogbölite') from Skogböl, Kimito, Finland (A. Nordenskiöld, 1857). II, Grizzly Bear Gulch, Black Hills, South Dakota (W. P. Headden, Amer. J. Sci. 1891, 41, 98). III, Greenbushes, Western Australia (E. S. Simpson, Rep. Austr. Assoc. Adv. Sci. 1908, 11 (for 1907), 442; and Chem. News, 1909, 91, 49). IV, Manganotantalite from Wodgina, Western Australia (E. S. Simpson, *l.c.*). V, Manganotantalite from Finnis river, North Australia (Rep. Govt. Geologist, South Australia, 1905).

	I. ¹	II.	III. ²	IV.	V.
Ta_2O_5	84.44	82.23	80.61	69.95	55.52
Cb_2O_5	—	3.57	2.50	14.47	24.92
SnO_2	1.26	0.32	1.51	0.36	4.40
FeO	13.41	12.67	10.89	2.68	2.72
MnO	0.96	1.33	3.78	(12.54)	11.16
Total	100.36	100.12	100.48	100.00	98.72
Sp.gr.	7.85	8.20	7.74	7.09	—

References.—Occurrence and Uses of Tantalum, Bull. Imp. Inst. London, 1907, 5, 429. For Australian occurrences, see E. S. Simpson, *l.c.* and 1910, 12 (for 1909), 310. L. J. S.

TANTALUM. Sym. Ta. At.wt. 181.8 (Chapin and Smith). Cf. Scars and Balke (J. Amer. Chem. Soc. 1915, 37, 833). Shortly after the discovery of columbium by Hatchett, in 1801–2, a metal of similar properties was detected by Ekeberg in certain Swedish minerals resembling those from which columbium had been isolated, and was called by him tantalum, on account of its extreme resistance to acids. Notwithstanding the fact that tantalite, the mineral which gave the largest yield of the new

¹ Also CuO , 0.14; CaO , 0.15.

² Also TiO_2 , 0.71; WO_3 , 0.13; H_2O , 0.14; NiO , 0.02; MgO , 0.19.

metal, was much heavier than columbite, Wollaston in 1809 concluded that the two metals were identical, and for many years they were indifferently termed columbium or tantalum. The similarity between the compounds of these metals, their invariable occurrence together in minerals, and the difficulty experienced in separating them from each other and the associated metals, prevented the large amount of work which was done upon them from yielding conclusive results, and it was not until the middle of the century that their true relations were established.

Although belonging to the group which includes vanadium, phosphorus, arsenic, antimony, bismuth, and nitrogen, tantalum and columbium have few properties in common with those elements, and they invariably occur with minerals belonging to entirely different groups. Commercially speaking, they are members of a group of heavy metals, which includes tungsten, molybdenum, and uranium, found only in the oldest plutonic rocks. These metals are characterised by the power of improving and hardening steel when added in extremely small quantities, and it is interesting to note that the minerals carrying them commonly contain the metals of the rare earths, and rare alkaline earths, or are associated with minerals containing them. Zirconium, thorium, cerium, and even lithium, together with practically all the other rare earths and alkaline earths, occur in the same parent rocks, and it is probable that this common, indeed almost invariable association, is intimately connected with the origin of these metals.

The use of tantalum and columbium for hardening steel, their high melting-points, and the possibility of working the pure metals, either alone or in alloy with each other, into wire, and vessels of great acid-resisting properties, have recently given an impetus to the search for minerals containing them, which has resulted, for the moment, in the working of more deposits than the market can utilise. There is little doubt, however, that the larger output will ultimately result in an increased demand, as the uses to which the metals can be applied are so numerous. The value of apparatus made from these metals for chemical, physical, and surgical purposes is undoubted, and is likely to result in a demand for even larger quantities of the mineral than are at present available.

For the use of tantalum as an electrode, *see* Wegelin (Chem. Soc. Abstr. 1913, ii. 880); *see also* Brunck (*ibid.* 1914, ii. 482).

As regards the occurrence of tantalum in nature, the article on COLUMBIUM may be consulted. The two metals occur together and, although one may predominate in a mineral to an extent which renders it the characteristic metal, it is extremely exceptional to find one without a considerable proportion of the other. For references to methods of analysing and separating them, *see* COLUMBIUM. *Cf.* Schoelle and Powell, Chem. Soc. Trans. 1921, 119, 1927.

The most satisfactory method for the determination of tantalum and columbium in minerals consists in fusion of the mineral with sodium bisulphate and separation of the columbium and tantalum by means of the potassium double fluorides (C. Wenzel, Anal. Assoc. Quim.

Argentina, 1923, 11, 297; J. Soc. Chem. Ind. 1924, 43, B. 620).

Detection of columbium and tantalum.—The finely-divided mineral is fused with potassium hydroxide, the fused mass dissolved in twenty times its weight of water, and the solution filtered, the insoluble portion being washed with warm, dilute potassium hydroxide solution. The titanium remains insoluble as K_2TiO_3 , along with iron and aluminium hydroxides, &c. The alkaline filtrate is treated with concentrated sodium hydroxide solution, when sodium tantalate crystallises in needles within a few minutes, if the liquid is now decanted, sodium columbate will separate out after several hours. Sodium columbate, when treated with ammonium oxalate, an acid, and zinc, gives a deep brown coloration, which changes to yellow as the reduction proceeds; the coloration is not changed by the addition of hydrogen peroxide. Titanium solutions treated in a similar way give a yellow coloration, which changes to orange-red with hydrogen peroxide. When potassium hyposulphite is added to an acid solution of columbic acid, a yellow precipitate forms; titanium solutions yield an orange-red coloration with this reagent. Columbic acid gives an orange precipitate with pyrogallol, provided the solution does not contain an excess of mineral acid; tantalum gives a pale yellow precipitate. Concentrated sulphuric acid solutions of columbium yield characteristic colour reaction with certain phenols, but only yellow colorations are obtained in the case of tantalum. The reaction of titanium described by Lenher and Crauford (Chem. Soc. Abstr. 1913, ii. 250) is rendered more sensitive by the addition of thiocyanate after reducing with zinc and hydrochloric acid (Moir, Chem. Soc. Abstr. 1916, ii. 348).

In the estimation of tantalum, the precipitate of tantalic acid usually contains some silica, and if this is removed by means of hydrofluoric acid, some of the tantalic acid is also lost. The tantalic acid may, however, be volatilised in a current of hydrogen chloride at 900° . The silica which is left is weighed, and the weight deducted from that of the original precipitate (Travers, Compt. rend. 1918, 166, 494; Chem. Soc. Abstr. 1918, ii. 177).

For the estimation of tantalum in alloy steels, *see* Kelley, Myers, and Illingworth (Chem. Soc. Abstr. 1917, ii. 546).

For the separation of tantalum by potassium chloride in hydrofluoric acid solutions, *see* Meimberg and Winzer (*ibid.* 1913, ii. 348); *see also* Merrill (*ibid.* 1922, ii. 230).

For many purposes, it is probable that an alloy of tantalum and columbium is suitable, but it is usual to separate the oxides or salts before reduction to metal, and, as tantalum is preferred for most purposes, it is fortunate that its proportion in the minerals now worked largely predominates. Like columbium, tantalum occurs in nature only as the pentoxide, and all the minerals in which it is found may be regarded as tantalates or, in a few rare minerals as silico-tantalates.

Although tantalum occurs as an essential, or at any rate invariable, constituent in a large number of the heavy rare minerals, the only one which is worked commercially is tantalite, essentially a tantalate of iron and manganese

$\text{Ta}_2\text{O}_5(\text{FeMn})\text{O}$, which may contain as much as 84 p.c. of Ta_2O_5 , although seldom exceeding 70 p.c. The proportion between the iron and manganese varies considerably, and the tantalum may be largely replaced by columbium. In other words, tantalite may emerge into *skogbolite* $\text{Ta}_2\text{O}_5 \cdot \text{FeO}$, containing up to about 85 p.c. of Ta_2O_5 , *manganotantalite* $\text{Ta}_2\text{O}_5 \cdot \text{MnO}$ (up to 85 p.c. Ta_2O_5), *tapiolite* $\text{Ta}_2\text{O}_5 \cdot \text{Cb}_2\text{O}_5 \cdot \text{FeO}$ (up to 74 p.c. of Ta_2O_5), *strüvertie*, an isomorphous mixture of iron tantalate and rutile, containing 36 p.c. tantalic oxide, and other minerals containing widely varying proportions of Ta_2O_5 , Cb_2O_5 , FeO , and MnO . On reference to the article on TUNGSTEN, it will be seen that similar variations occur in the composition of wolfram, the tungstate of iron and manganese.

To obtain tantalum, tantalite, containing at least 60 p.c. of the oxide and only a few per cent. of columbium oxide is pulverised, fused with potassium hydroxide, and the filtered solution of the product treated with nitric or sulphuric acid, thus precipitating the insoluble acid oxides of tantalum and columbium, which, after washing, are dissolved in hydrofluoric acid and converted into double potassium fluorides, which can be readily separated from one another by crystallisation.

Tantalum also occurs as an apparently essential, although highly variable, constituent of between thirty and forty other minerals, including *microlite* $\text{Ta}_2\text{O}_5(\text{CaO})_2$, containing up to about 70 p.c. of Ta_2O_5 ; *fergusonite*, a tantalate and columbate of yttrium, erbium, cerium, &c. (up to 43 p.c. Ta_2O_5); *yttrotantalite*, a tantalate and columbate of various rare earths (up to 47 p.c. Ta_2O_5); and *stibiotantalite*, a tantalate and columbate of antimony (up to 51 p.c. Ta_2O_5). Other minerals containing tantalum are as follows: *cassiterite*, *columbite*, *mossite*, and *rutile*.

The principal localities where tantalum minerals occur have been detailed in the article on COLUMBIUM. At the present time, the main supply is obtained from Greenbushes, Pilbara, Wodgina, and elsewhere in Western Australia, where it occurs with tinstone and wolfram, partly in isolated masses which have escaped denudation during the weathering of the surrounding rocks, and largely in the form of alluvial material.

Metallic tantalum may be prepared in an impure state by reducing potassium tantalo-fluoride with potassium or sodium, or by reducing the pentoxide in the electric furnace with carbon. It was first prepared in a pure state by von Bolton, by reducing the tantalo-fluoride ($\text{TaF}_5 \cdot 2\text{KF}$) with sodium and melting the washed, impure powder *in vacuô* in the electric furnace. The fusion *in vacuô* in the electric furnace being repeated with modifications to remove all traces of impurity, and the preparation of the tantalo-fluoride being so conducted as to ensure its purity and freedom from columbium. The fusion *in vacuô* removes all traces of occluded gases, including the hydrogen and the oxygen (in the form of gas and of oxide) produced by the oxidation of the crude metal during the washing (cf. U.S. Pats. 958180, 974835; see Eng Pat. 24234 of 1906).

Metallic tantalum in a powdered form is

obtained by heating the double fluoride of potassium and tantalum with metallic sodium or potassium in an evacuated tube. After the impurities have been removed by washing with water, the powder is compressed and finally fused in a vacuum electric furnace. The resulting product has a purity of 99.5 p.c., m.p. 2850°C ., a linear expansion slightly less than that of platinum, a high electrical resistance, and is characterised by its toughness and great ductility and malleability. Hydrochloric, nitric, and weak sulphuric acids, either hot or cold, and solutions of caustic alkalis do not attack the metal. Hot concentrated sulphuric acid attacks it slowly and hydrofluoric acid also only attacks it slowly if both metal and acid are pure. A mixture of hydrofluoric and nitric acids will attack the metal with avidity. It is suggested that the metal will be suitable for the manufacture of dental and surgical instruments, and on account of the avidity with which it combines with hydrogen, oxygen, and nitrogen, for the manufacture of vacuum tubes for radio sending and receiving instruments. It is also suggested that it can be used in the manufacture of electrolytic valves where, on account of its resistance to chemical corrosion, it will be superior to magnesium and aluminium (G. W. Balke, Chem. & Met. Eng. 1922, 27, 1271-1273; J. Soc. Chem. Ind. 1923, 42, 608 A).

Another method of preparing the metal devised by von Bolton consists in passing an electric current through rods of tantalum tetroxide Ta_2O_4 *in vacuô*. The intense heat produced by the current results in the expulsion of the oxygen and the production of brittle rods of impure metal which may be converted into pure tantalum by fusing and re-fusing *in vacuô* in the electric furnace as above. The tantalum tetroxide is prepared by shaping rods from a paste made of tantalum pentoxide and paraffin, and calcining them. The resultant metal possesses the same qualities as that made from the tantalo-fluoride, but the method is not employed on a commercial scale.

Wrought tantalum is a white metal, somewhat less bright than platinum, and usually showing a bluish tarnish from superficial oxidation. It has a sp.gr. of 16.8 (von Bolton); a specific heat, between 14° and 100° , of 0.033 (Dewar); and a m.p. of 2250° - 2300° (von Bolton); $2850^\circ \pm 40^\circ$ (Pirani and Meyer, Ber. 1911, 13, 540); 2798° according to tests made in 1912 at the University of Wisconsin. Its linear thermal coefficient of expansion between 0° and 60° is 0.0000079 according to tests made by the Imperial Standards Committee. It is about as hard as soft steel, but possesses a greater strength, the drawn wire having a tensile strength of 93 kilos. per sq. mm. as against 80 kilos. for good steel. The compressibility of tantalum expressed in the megabar standard $\times 10^6$ (Chem. Soc. Abstr. 1904, ii. 385) is 0.54 (Richards and Bartlett (J. Amer. Chem. Soc. 1915, 37, 470)).

For the spectrum of tantalum, see Siegbahn and Friman (Chem. Soc. Abstr. 1916, ii. 362; ii. 405). Accurate measurements have been made of the wave-lengths of lines in the arc spectrum of tantalum between $\lambda 7000$ and $\lambda 2430$. The observations, which are compared with those obtained previously by Exner and Haschet, also

afford information relative to the intensity and the sharpness of the lines.

There is no evidence of the occurrence of pairs of lines with a constant difference of frequency as suggested by Paulson (*cf.* Chem. Soc. Abstr. 1915, ii. 196); Josewski (Chem. Soc. Abstr. 1918, ii. 25).

The potential differences between tantalum and a solution of tantalum pentafluoride (0.006 mol.) were measured both with passive tantalum and active tantalum. The values $\text{Ta}(\text{passive})/\text{TaF}_5 = +1.537$ volt, and $\text{Ta}(\text{active})/\text{TaF}_5 = +0.165$ volt were obtained ($H=0$).

Von Hevesy and Slade (Zeitsch. Elektrochem. 1912, 18, 1001) arrived at the conclusions, that in its most passive condition tantalum has a nobler potential than silver of about 1 volt, whilst active tantalum has a potential close to that of copper (Chem. Soc. Abstr. 1913, ii. 13).

Tantalum is more malleable and ductile than columbium. It becomes progressively softer when heated, and can be hammered, rolled, or drawn into wire or seamless tubes similarly to steel, and is readily worked at a red heat (*cf.* Eng. Pat. 19962, 1910). When heated in air, powdered tantalum readily oxidises, and both powder and thin wire burn at a red heat, the former with incandescence. Sheets of tantalum acquire a yellow tarnish at about 400° and, slowly at 500° or rapidly at 600° , become bluish, as in the case of steel when being tempered.

The worked metal possesses an extraordinary combination of toughness and hardness, and the slight superficial oxidation which is produced during working or by heating, enormously increases its property of resisting abrasion. So much is this the case that a diamond drill has but little penetrative power, although the metal is still capable of being rolled or drawn; the specially prepared metal has been found effective for the manufacture of pen nibs in place of iridium-pointed pens.

Tantalum has been suggested as a suitable substitute for iridio-platinum in the construction of standard weights, as it has been found to satisfy the necessary requirements of permanence and hardness. It is also suitable as a substitute for platinum for cathodes, especially for electroanalysis, and in the electrolysis of alkali chloride solutions for the manufacture of hypochlorites (bleaching solutions). *Cf.* Oesterheld, Zeitsch. Elektrochem. 1913, 19, 585; Brunck, Chem. Zeit. 1914, 38, 565.

At a dull red heat, tantalum absorbs large quantities of hydrogen or nitrogen. At a yellow heat, about 740 volumes of hydrogen are thus absorbed. The metal is rendered brittle and fragile by the presence of either gas, but both can be expelled *in vacuô*. Three-fourths of the hydrogen can be driven off by heating to redness *in vacuô*, but the remainder can only be expelled by fusing *in vacuô* in the electric furnace, a treatment to which all metal now made is exposed, with a view to expelling all occluded gases and such other impurities as are volatile at the temperature at which tantalum melts (*cf.* Sieverts and Bergner, Ber. 1911, 44, 2394).

The presence of occluded gases or small quantities of impurities completely alters the character of the metal, the value of which for all

purposes to which it can be applied *as metal*, depends entirely on the extreme care taken in its purification after the preliminary stages of manufacture. The presence of even less than 0.1 p.c. of carbon renders it brittle, and it may be mentioned that the brittle metal obtained by Moissan in the electric furnace contained 0.5 p.c. The metallic nitride TaN , first prepared by Rose, is metallic in appearance, and was thought by him to be the metal itself.

Wrought tantalum is peculiarly resistant to all acids except hydrofluoric acid. It is absolutely unattacked by *aqua regia* even with prolonged boiling, and is not affected by organic acids or by the healthy or morbid secretions of the body, so that it is highly suited for the manufacture of dental and surgical instruments. Its extreme hardness permits of its use in place of steel, and the absence of corrosion and consequent ease of cleansing are resulting in an increased demand for such purposes.

Tantalum is readily attacked by fused caustic alkalis or alkaline nitrates and by sulphur. It alloys with iron, tungsten, molybdenum, and many other metals, but few of the alloys are of commercial importance excepting ferro-tantalum.

Ferro-tantalum is commonly prepared by the direct reduction of tantalite in the electric furnace, and is used to a small, but apparently increasing, extent in steel manufacture, for purposes similar to those for which ferro-tungsten, ferro-molybdenum, and ferro-vanadium are employed. The alloy commonly contains up to 50 p.c. of tantalum and columbium, the proportion of the latter being comparatively low and depending upon the amount which was present in the original tantalite. An alloy of 80 parts of iron or steel with 10 of nickel and 10 of tantalum, possesses great strength, elasticity and hardness (Siemens und Halske, D. R. P. 282575, 1913). Platinum tantalum alloys (0.5–20 p.c. Ta) possess in a high degree the properties of platinum-iridium; the relative quantities of tantalum and iridium required to produce the same degree of hardness and mechanical resistance in platinum are as 1 : 5 (Eng. Pat. 477270, 1914).

Tantalum was the first metal to be used in commercial quantities for the manufacture of filaments. Its value depends on its great electrical resistance and high melting-point, and upon the fact that it can be drawn down to extremely fine wire (less than 0.03 mm.). The National Electric Lamp Association of the United States, in 1910 employed nearly five million feet of tantalum wire weighing under 100 lbs. for the manufacture of filaments.

According to Messrs. Siemens and Halske, taking the normal type of electric filament lamp of 25 c.p. at 110 volts, the filament for a lamp measures 650 mm., and has a diameter of 0.05 mm., so that 45,000 lamps could be made from 1 kilo. of wire. This number is now largely exceeded, as it has been found possible to considerably reduce the diameter of the wire.

The electrical resistance (cold) of tantalum wire is 0.165 ohm per metre length of 1 sq. mm. section. When loaded to 1.5 watt per candle, the resistance of the same wire rises to 0.830 ohm.

Platinum-tantalum alloys containing up to 20 p.c. Ta are resistant to acids and fused potassium bisulphate, and are more resistant

to *aqua regia* than platinum itself. These alloys have greater hardness than the corresponding Pt-Ir alloys and are less expensive. The hardness of platinum is increased 25 p.c. by the addition of 1 p.c. Ta and 40 p.c. by 2 p.c. Ta. The alloys may be prepared by adding tantalum in the form of compressed pastilles to molten platinum or by fusing together spongy platinum and tantalum contained in a zirconia crucible in a resistance furnace. The malleability of the alloys decreases with increasing percentages of tantalum (L. Duparc, Eng. Pat. 200074, June 8th, 1923; Conv., June 27th, 1922; J. Soc. Chem. Ind. 1924, 43, B, 388). G. T. H.

COMPOUNDS OF TANTALUM.

Tantalum tetroxide Ta_2O_4 , a porous dark-grey mass which scratches glass, is formed when the pentoxide is heated with magnesium in a carbon crucible. When powdered it is dark brown. It is not attacked by acids, but with chlorine gives a white readily volatile sublimate containing 18.5 p.c. chlorine. When heated it burns forming the pentoxide (Smith and Maas, Zeitsch. anorg. Chem. 1894, 7, 96).

Tantalum pentoxide Ta_2O_5 occurs in nature as the various *tantalites*, from which it may be obtained by fusing the finely-powdered mineral with three times its weight of acid potassium sulphate. For production of tantalic acid from West Australian fergusonite, see Wedekind and Maass (Zeitsch. angew. Chem. 1910, 23, 2314; J. Soc. Chem. Ind. 1911, 25). The mass is boiled with water, and the residue is digested with ammonium sulphide, thus removing tin and tungsten and converting iron into sulphide. The residue is then washed and boiled with dilute hydrochloric acid and filtered; the mass consisting of the hydroxides of tantalum and columbium, and of titanic acid and silica, is washed with boiling water, dissolved in hydrofluoric acid, filtered, and heated to remove silicon fluoride; potassium fluoride is added to the solution which is then concentrated. The potassium tantalofluoride separates first; it is well washed, recrystallised, and heated to 400° with its own weight of concentrated sulphuric acid. The residue when boiled out with water gives the oxide and sulphuric acid. The acid adhering to the oxide may be removed from the oxide by heating with ammonium carbonate (Krüss and Nilson, Ber. 1887, 20, 1676; Moissan, Compt. rend. 1902, 134, 212). A more complete separation, which may be used for the estimation of tantalum, is described by Weiss and Landecker (D. R. P. 221429). The substance is fused with alkali bisulphite and the mass lixiviated with water. The solution is treated with sulphurous acid and boiled, when the tantalic, columbic, and titanic acids are precipitated quantitatively together with some tin, if present. The latter is removed by means of ammonium sulphide solution, and the residue is fused with a slight excess of sodium carbonate, and a small quantity of sodium nitrate is added towards the end of the operation, the mass being then gently heated until the nitrate is decomposed. The product is boiled with water and filtered from the titanium compound. After removing small quantities of the latter still present in the solution, it is treated

with carbon dioxide or with a bicarbonate, whereby tantalic acid is precipitated quantitatively and, when heated to low redness, yields the pentoxide (D. R. P. 221429; J. Soc. Chem. Ind. 1910, 696; see also Zeitsch. anorg. Chem. 1909, 64, 65; Chesneau, Compt. rend. 1909, 149, 1132; also art. COLUMBIUM). Tantalum pentoxide is formed when the metal is treated with oxygen (Muthmann, Weiss and Riedelbauch, Annalen, 1907, 355, 58).

Tantalum pentoxide is a white amorphous, infusible powder, which, when strongly heated, becomes crystalline. It may also be obtained in rhombic prisms by heating it with boron trioxide or melting it with microcosmic salt. Its sp.gr. varies with the intensity of the heat to which it has been subjected, and ranges from 7.055 to 8.257 (Marignac, Ann. Chim. 1866, [iv.] 9, 249). The ignited pentoxide is insoluble in acids, and is not acted on by hydrogen, but it may be reduced by heating strongly with carbon in the electric furnace. It forms double compounds with magnesium and the alkalis of the type $MgMTaO_8 \cdot xH_2O$ (M =alkali metal) (Balke and Smith, J. Amer. Chem. Soc. 1908, 30, 1637).

Tantalum pentoxide is stable towards light, but becomes markedly photosensitive in the presence of suitable media. Reaction is due to reduction. This is the more remarkable, since the oxide is reducible by purely chemical means with considerable difficulty (Renz, Chem. Soc. Abstr. 1922, ii. 61).

Tantalic acid $HTaO_3$ may be obtained as above or by mixing the chloride with water when it forms a gelatinous mass, which, when exposed to air, and then mixed with water containing ammonia, forms a crystalline powder. It is soluble in hydrofluoric, oxalic, and citric acids, but not in alkaline carbonates (Berzelius, Ann. Chim. [ii.] 3, 140). Pure tantalic acid has been shown to be non-volatile when heated in oxygen or on evaporation of its solution in hydrogen fluoride, and new double fluorides of tantalum with hydrogen, ammonium, and barium are described by O. Hahn and K. F. Puetter (Zeitsch. anorg. Chem. 1923, 127, 153; Chem. Soc. Abstr. 1923, ii. 773). For the hydrosols of tantalic acid, see Hanser and Lewite (Zeitsch. angew. Chem. 1912, 25, 100).

Estimation of tantalic acid and columbic acid in tantalites, columbites, yttrotantalites, and fergusonites, and the colorimetric estimation of columbium.—The principle of the method is as follows: The mineral is decomposed by fusion with potassium hydrogen sulphate. The fused mass is digested with hydrochloric acid, the residue of mineral acids neutralised with ammonia, and then digested with ammonium sulphide at a gentle heat for 24 hours. The residue is collected, washed successively with hot water and boiling dilute hydrochloric acid, and then dissolved in excess of hydrofluoric acid. The tantalum is then precipitated as potassium tantalum fluoride, K_2TaF_7 , by the addition of a concentrated solution of potassium hydrogen fluoride, the columbium remaining in solution. The filtrate from the precipitate is evaporated to dryness, digested with strong sulphuric acid, boiled with water to remove the sulphuric acid, dissolved in hydrofluoric acid, and again precipitated with potassium hydrogen

fluoride in order to remove any tantalum still remaining. This process is repeated until the tantalum is completely separated from the columbium. The potassium tantalum fluoride is then converted into the pentoxide and weighed as such. It generally contains some titanium, which must be estimated colorimetrically. For the estimation of the columbium, all the hydrofluoric acid filtrates are evaporated to dryness, and then again taken down with strong sulphuric acid. The residue is treated successively with boiling water, ammonia, ammonium sulphide, and very dilute hydrochloric acid, and weighed as columbium pentoxide.

Gallotannic acid has hitherto been used in testing colorimetrically for columbic acid, but the colour is affected considerably by the presence of tantalum. Meimberg (Zeitsch. angew. Chem. 1913, 26, 83) makes use of the fact that the columbates, especially the fluoride compounds, are reduced by tin and hydrochloric acid to coloured products, whereas the tantalates are not affected. The potassium tantalum fluoride, which is to be tested for columbium, is dissolved in dilute hydrochloric acid containing some hydrofluoric acid, and the solution evaporated down until a copious precipitation of potassium tantalum fluoride has occurred. After cooling, the crystals are collected and washed with cold dilute hydrofluoric acid. The columbium, together with some tantalum, is in the filtrate, which is evaporated to dryness on the sand-bath. The residue is dissolved in concentrated hydrochloric acid, the solution placed in a colorimeter tube, and reduced with tin. The reduction is complete in about 15 minutes and the colour is then compared with that of a standard, which must be freshly made for each determination. The solutions to be estimated, as also the standard, should not contain more than 0.1 p.c. of columbium. By this method 0.01–0.005 p.c. of columbium can readily be estimated (Chem. Soc. Abstr. 1913, ii. 251).

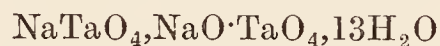
For the separation of titanitic, tantalic, and columbic acids from most other elements, a method was given by Weiss and Landecker (Chem. Soc. Abstr. 1909, ii. 942), which consisted in dissolving the acids, whether precipitated from acid or basic solutions, in hydrogen peroxide and reprecipitating by boiling the solution with sulphurous acid. Experiments on the solubility of these acids in acid solutions of hydrogen peroxide have not confirmed Weiss and Landecker's statements. The acids used for the experiments were prepared by fusing the commercial material with sodium hydrogen sulphate, extracting with boiling water, and hydrolysing the solutions by boiling with sulphurous acid. Titanitic and columbic acids are practically completely soluble in acid hydrogen peroxide, but tantalic acid when precipitated hot is almost insoluble, and when precipitated cold is only partly soluble. In mixtures, the different acids influence one another differently, according to the conditions. Tantalic acid lowers the solubility of columbic acid, whilst titanitic acid may increase the solubility of tantalic acid or may itself be rendered less soluble. Experiments with the ultra-microscope indicate that, in acid hydrogen peroxide solutions, titanitic acid forms a true

solution, whilst columbic and tantalic acids form colloidal solutions (Hahn and Gille, Zeitsch. anorg. Chem. 1920, 112, 283; Chem. Soc. Abstr. 1920, ii. 763).

Tantalates.—For some naturally occurring tantalates and their extraction, see Rammelsberg, Chem. Soc. Trans. 1872, 25, 189. They are all insoluble, and are mostly derivatives of the above acid. In addition, *hexatantalates* are known of the formula $M_3Ta_6O_{19}, xH_2O$, the alkali salts of which are soluble in water, and may be obtained by dissolving the acid in alkali hydroxide, or by fusing the pentoxide with the alkali hydroxides or carbonates. When tantalum pentoxide is heated with the chlorides of calcium, magnesium and other metals, crystalline tantalates of these metals are formed (Joly, Compt. rend. 1875, 81, 266, 1266).

Pertantalic acid $HTaO_4, nH_2O$ is obtained by treating its potassium salt with dilute sulphuric acid. It is a white powder, fairly stable, decomposed only above 100° , but resembling per-columbic acid in other respects.

The *potassium salt* $K_3TaO_5, \frac{1}{2}H_2O$ is obtained by fusing tantalum pentoxide with potassium hydroxide, the mass is extracted with a little water, filtered, warmed with a little hydrogen peroxide, filtered, precipitated with alcohol, and the precipitate after washing with alcohol and ether, is treated with hydrogen peroxide and potassium hydroxide, and finally reprecipitated with alcohol. The corresponding sodium and barium salts, also the potassium calcium salt $KCaTaO_5, 4\frac{1}{2}H_2O$, and the sodium salt



have also been prepared by treating the corresponding tantalate with hydrogen peroxide (Melikoff and Pissarjewsky, Zeitsch. anorg. Chem. 1899, 20, 340; Balke, J. Amer. Chem. Soc. 1905, 27, 1155; Balke and Smith, *l.c.*).

Tantalum pentachloride $TaCl_5$, obtained by heating a mixture of the pentoxide and carbon in a current of chlorine, or by heating the oxide in a quartz tube to redness in a stream of chlorine and carbon tetrachloride, or in the vapour of carbonyl chloride, forms light yellow needles, m.p. 211° , b.p. $241.6^\circ/753$ mm., and volatilise at 144° (Deville and Troost, Compt. rend. 1867, 64, 294; see Willgerodt, J. pr. Chem. 1887, [ii.] 35, 391; Hermann, *ibid.* 1872, [ii.] 5, 66).

Preparation and properties.—According to Hampe (Chem. Soc. Abstr. 1888, 211), tantalum pentachloride is a good conductor, whilst columbium pentachloride is an insulator. To test the accuracy of these observations the two pentachlorides have been prepared in such a manner that moisture was altogether excluded and the substance was distilled out of contact with air directly into the conductivity apparatus. The tantalum pentachloride was prepared by passing chlorine over a heated mixture of tantalum pentoxide and sugar carbon and distilling the pentachloride. It formed a snow-white mass of crystals which, when melted at 230° – 240° , had a conductivity $K = 0.30.10^{-6}$. The platinum electrodes were strongly attacked, but the liquid appeared clear and unchanged, Columbium pentachloride was obtained by passing a current of chlorine over columbium sulphide, and, after removal of the sulphur

chloride, distilling the columbium pentachloride. It crystallised in long, yellow needles, and its conductivity at 220° – 235° was $K.=0.22.10^{-6}$. The electrodes were attacked also in this case. The two compounds are therefore both insulators of about the same order as the best conductivity water (Biltz and Voigt, *Zeitsch. anorg. Chem.* 1921, 120, 71; *Chem. Soc. Abstr.* 1922, ii. 302).

Tantalum pentachloride is reduced by metallic aluminium in the presence of aluminium chloride at 300° to a mixture of various chlorides of tantalum. A larger excess of aluminium remains unchanged even when, as is occasionally the case, metallic tantalum is formed. The temperature is limited by the resistance of the tubes. The dark green product of the reaction evolves aluminium chloride and tantalum pentachloride when heated, the latter being given off in such manner that the composition of the residue can be regulated by the choice of temperature and pressure. A mixture corresponding approximately with tantalum tetrachloride is obtained at $250^{\circ}/2$ –3 mm.; at 350° – 400° the residue has the composition of a trichloride, which is itself decomposed at about 500° , leaving a mixture of di- and tri-chlorides.

The mixtures of chlorides are moderately stable towards air. Treatment with water causes the formation of intensely green solutions of the trichloride, whilst the pentachloride is hydrolysed to hydrochloric and tantalic acids and the dichloride remains undissolved as a blackish-green residue. The green solutions become oxidised slowly on exposure to air, the action being checked by the presence of acids. The di- and tri-chlorides are soluble in cold, sufficiently dilute sodium hydroxide solutions without evolution of hydrogen or alteration in the valency of the element. The alkaline solutions are oxidised with unusual readiness by air and evolve hydrogen when they are warmed; a brown tantalous oxide is thereby produced, as an intermediate step in the formation of tantalic acid. The production of this substance is also observed during rapid oxidations (with hydrogen peroxide or nitric acid) in acid solution. When oxidation is effected by hydrogen peroxide in alkaline solution, a brown solution of a per-tantalate is obtained, which evolves oxygen and becomes colourless when boiled (Ruff and Thomas, *Ber.* 1922, 55, [B] 1466; *Chem. Soc. Abstr.* 1922, ii. 513).

On heating the pentachloride with powdered aluminium, or preferably zinc, and extracting with hydrochloric acid, it yields $\text{HTa}_3\text{Cl}_7, 4\text{H}_2\text{O}$ as a blackish-green, stable crystalline powder (Lindner and collaborators, *Ber.* 1922, 55, [B] 1458).

Experiments made with carefully purified tantalum chloride show that it is quite stable in an atmosphere of dry nitrogen or air, that it does not occlude chlorine, but that it undergoes hydrolysis in an atmosphere which has not been thoroughly dried by means of phosphoric oxide. On account of the readiness with which hydrolysis occurs, Sears (*J. Amer. Chem. Soc.* 1917, 39, 1582) considers that tantalum chloride is not suitable for use in atomic weight determinations (*Chem. Soc. Abstr.* 1917, ii. 481).

Tantalum pentabromide TaBr_5 can be prepared by passing bromine vapour over a strongly heated mixture of freshly-ignited tantalic oxide

and pure sugar-carbon, air having been previously removed by heating the mixture in a current of dry carbon dioxide. It forms long yellow plates, m.p. about 240° , b.p. about 320° , fumes in moist air and reacts readily with methyl and ethyl alcohols.

Bromotantalum bromide $\text{HTa}_3\text{Br}_7, 4\text{H}_2\text{O}$ has been obtained by reducing the pentabromide with sodium amalgam. It forms minute, black, hexagonal prisms giving a dark green powder. It is very stable and has tinctorial properties. A very minute quantity of the bromide is sufficient to give a beautiful emerald green colour to a considerable quantity of water and the solution imparts a stable pale-green colour to silk. Only two of the bromine atoms are in the ionic condition. When treated with caustic soda it is transformed into the *hydroxide* $\text{HTa}_3\text{Br}_6(\text{OH}), 4\text{H}_2\text{O}$, thin hexagonal plates, which, on treatment with hydrochloric acid, gives the *chloride* $\text{HTa}_3\text{Br}_6\text{Cl}, 4\text{H}_2\text{O}$. The *iodide* $\text{HTa}_3\text{Br}_6\text{I}, 4\text{H}_2\text{O}$ and the *chlorotantalum chloride* $\text{HTa}_3\text{Cl}_7, 4\text{H}_2\text{O}$ have also been prepared (Chapin, *J. Amer. Chem. Soc.* 1910, 32, 323; Lindner (*l.c.*)).

Tantalum pentaiodide TaI_5 can be prepared by heating the bromide in a current of hydrogen iodide. It forms almost black plates, melts to a dark brown liquid, can be distilled in a current of carbon dioxide and fumes in moist air (van Haagen, *J. Amer. Chem. Soc.* 1910, 32, 729).

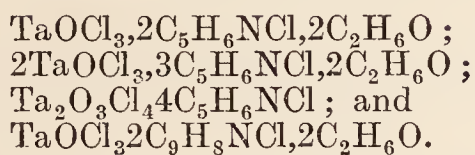
Tantalum pentafluoride TaF_5 is obtained by subjecting dry roughly powdered warmed tantalum contained in a boat inserted in a platinum tube, to the action of fluorine, or by treating the pentachloride with anhydrous hydrogen fluoride in a freezing mixture in a platinum apparatus. The pentafluoride is purified by distilling it *in vacuô* at about 90° – 100° . It forms colourless, strongly refractive prisms, $D^{19.5}=4.744$, m.p. 96.8 (corr.), b.p. 229.2° – 229.5° (corr.), is very hygroscopic and is readily soluble in water. Caustic soda or ammonia precipitate tantalic acid containing a little fluorine from the solution. The fluoride attacks glass slowly at ordinary temperature, but rapidly when heated (Ruff, Zedner, Schiller, and Heinzelmann, *Ber.* 1909, 42, 492; Ruff and Schiller, *Zeitsch. anorg. Chem.* 1911, 72, 329).

Tantalum pentafluoride forms a number of double fluorides with other metals (Balke, *l.c.* 1140; Smith, *Chem. Zentr.* 1905, ii. 1160; Ephraim and Heymann, *Ber.* 1909, 42, 4456), of which the

Potassium tantalofluoride $2\text{KF}, \text{TaF}_5$ is the most important. It is formed by bringing the two fluorides together in a dilute aqueous solution of hydrofluoric acid and consists of small anhydrous needles. On standing hydrofluoric acid is evolved. It is much more soluble in hot than in cold water, but when the solution is boiled an insoluble oxyfluoride $\text{Ta}_2\text{O}_5 + 2(2\text{KF} \cdot \text{TaF}_5)$ is precipitated (Krüss and Nilson, *l.c.*). The reactions of tantalum potassium fluoride are given in tabular form by Hall (*J. Amer. Chem. Soc.* 1904, 26, 1235). Tantalum pentafluoride also forms double salts with pyridine and other organic bases.

The following tantalum double salts with pyridine and quinoline have been prepared by the action of the base on an alcoholic solution of

tantalum pentachloride containing hydrochloric acid



All these salts form colourless crystals soluble in alcohol, decomposed by water and becoming opaque on exposure to air (Weinland and Storz, *Zeitsch. anorg. Chem.* 1907, 54, 223).

Tantalum tetrasulphide Ta_2S_4 or TaS_2 may be prepared by passing a stream of sulphuretted hydrogen carrying carbon disulphide over tantalum pentoxide at 650° – 900° . It is a very stable body not decomposed at 1300° , is scarcely attacked by boiling acids, readily absorbs moisture, and commences to be transformed into a crystalline variety at 1200° (Biltz and Kircher, *Ber.* 1910, 43, 1636).

Tantalum nitride Ta_3N_5 is obtained by heating the metal to 1000° in nitrogen (Muthmann, Weiss and Riedelbauch, *Annalen*, 1907, 355, 58), or by passing ammonia over tantalum chloride heated to a temperature not above that at which ammonium chloride volatilises. It is an amorphous yellowish-red mass, which, when heated to whiteness in dry ammonia forms the black *nitride* TaN (Joly, *Compt. rend.* 1876, 82, 1195).

Tantalum silicide TaSi_2 crystallises in iron-grey prisms, sp.gr. 8.83, with a metallic lustre; is decomposed readily by fused alkalis, dissolves in hydrofluoric acid, reacts with fluorine when heated gently, and is oxidised when heated in a current of oxygen (Hönigschmid, *Monatsh.* 1907, 28, 1017).

TANTIRON, DURIRON, IRONAC, NARKI. Trade names for varieties of ferro-silicon used as acid-resisting metal.

TAP CINDER. The basic iron silicate constituting the slag and flowing through the tap-hole of the puddling furnace, *v.* IRON.

TAPHOSOTE *v.* SYNTHETIC DRUGS.

TAPIOCA. A product obtained from the starch of cassava (*q.v.*) *Manihot utilissima* (Pohl) and other species of *Manihot*, widely cultivated in the West Indies. There are two varieties—the sweet and the bitter. The kind principally grown is the bitter. Its juice yields *cassareep*, a valuable ingredient of the West Indian ‘pepper-pot,’ and a drink known as ‘Cassirie.’ Other products of cassava-roots are ‘cassava meal’ or conac, and cassava cake. Cassava starch is prepared by grating the roots and straining the suspended starch through cloth or wire gauze. The moist starch is heated and stirred until it agglutinates into little rounded, rugged masses, in which state it constitutes the tapioca of commerce. The starch granules become more or less swollen by this treatment, some of them preserving their original shape and character, while others gelatinise into shapeless or irregular masses. Tapioca usually contains from 10 to 14 p.c. of moisture with traces of nitrogenous matter and fat, but should be free from fibrous matter if properly prepared (Balland, *J. Pharm. Chim.* 1903, 17, 316).

The average of the analyses of seven samples

of commercial tapioca (*Bull. U.S. Dept. of Agric.* 28, 1899) gave :

Water	Protein	Fat	N-free extract	Crude fibre	Ash
11.4	0.4	0.1	87.9	0.1	0.1

H. I.

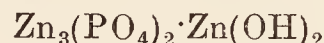
TAPIOLITE. Iron tantalate FeTa_2O_6 , crystallised in the tetragonal system and belonging to the following isodimorphous group of minerals :

	Orthorhombic	Tetragonal
FeTa_2O_6	Tantalite (<i>q.v.</i>)	Tapiolite
FeCb_2O_6	Columbite (<i>q.v.</i>)	Mossite

The tetragonal members are very similar in form and interfacial angles to rutile, cassiterite, and strüverite (*q.v.*). Owing to elongation in the direction of a pyramid edge and twinning, their crystals simulate an orthorhombic form very close to that of tantalite. This has given rise to some confusion; some of the material previously regarded as tantalite and ‘skogbölite’ being really twinned tapiolite. Tapiolite usually contains varying amounts of columbium isomorphously replacing tantalum, with a corresponding range in sp.gr. 7.22–7.91. Mossite is known only as such an intermediate member with $\text{Ta} : \text{Cb} = 1 : 1$ about, and sp.gr. 6.45 (sp.gr. calculated for pure mossite 5.20). These are black opaque minerals with a sub-metallic lustre and very similar in their characters to tantalite and columbite, from which, indeed, they can only be distinguished when good crystals are available. They occur in granite and pegmatite, often in association with cassiterite. Tapiolite is found at Tammela in Finland, in the Pilbara goldfield in Western Australia, at Custer in the Black Hills of South Dakota, and at Topsham in Maine. Mossite is from Moss and Sætersdal in Norway.

L. J. S.

TARBUTTITE. Basic zinc phosphate



containing Zn 53.9 p.c.; crystallised in the anorthic system. The crystals vary considerably in habit and appearance, but always show a prominent cleavage in one direction with pearly lustre. They are transparent and colourless or pale shades of yellow, red, or green. Sp.gr. 4.12; $\text{H.} = 3\frac{1}{2}$; readily soluble in dilute hydrochloric acid. Water is lost only at a red-heat; the material is then yellow while still hot, indicating the presence of basic zinc. The mineral is known only from the lead-zinc (cerussite and hemimorphite) mines at Broken Hill, in Northern Rhodesia, but it occurs there in some abundance. It is associated with other zinc phosphates, hopeite and parahopeite, and sometimes forms pseudomorphs after smithsonite and descloizite. Minute crystals encrusting bones in a cave indicate that the mineral is of recent formation (L. J. Spencer, *Min. Mag.*, 1908, 15, 1).

L. J. S.

TAR, COAL, v. COKE, FUEL and GAS COAL.

The Constituents of Coal Tar, by P. E. Spielmann, Longman's series of Monographs on Industrial Chemistry, edited by Sir Edward Thorpe.

For the estimation of phenol in mixtures of tar acids, see Hoffert (*J. Soc. Chem. Ind.* 1922, 41, 334, T; *Chem. Soc. Abstr.* 1922, ii. 878).

For the estimation of phenol in crude carboic acid and tar oils, see Weiss, *Chem. Soc. Abstr.* 1913, ii. 442.

TAR, WOOD, v. WOOD, DESTRUCTIVE DISTILLATION OF.

For the alcohols and bases of vacuum tar, see Pictet, Kaiser, and Labouchere (Compt. rend. 1917, 165, 113; Chem. Soc. Abstr. 1917, i. 515).

TARAXACUM. The air-dried fresh roots of *Taraxacum officinale*, Wiggers, contain a small amount of an enzyme capable of hydrolysing amygdalin, and (1) *p*-hydroxyphenylacetic acid $C_8H_8O_3$, m.p. 144° – 146° ; (2) 3:4-dihydroxycinnamic acid $C_9H_8O_4$, m.p. 214° – 216° ; (3) choline $C_5H_{15}O_2N$; (4) lævulose, yielding an osazone, m.p. 204° – 206° ; (5) a monohydric alcohol, *taraxasterol* $C_{25}H_{47}OH$, m.p. 221° – 222° , and a monohydric alcohol, *homotaraxasterol* $C_{25}H_{39}OH$, m.p. 163° – 164° , $[\alpha]_D +25.3^\circ$; (6) cluytanol $C_{29}H_{46}O(OH)_4$, m.p. 297° ; (7) palmitic, cerotic, and mellissic acids together with a mixture of unsaturated acids consisting chiefly of oleic and linolic acid with a little linolenic acid (Power and Browning, Chem. Soc. Trans. 1912, 101, 2411). According to these authors the bitter taste of taraxacum, hitherto ascribed to the so-called 'taraxacin,' is due chiefly to a dark-coloured amorphous material, and not to any distinct principle. The substances known as 'taraxacin' and 'taraxacerin' are indefinite substances and probably complex mixtures (cf. DANDELION ROOT).

TARRAGON OIL v. OILS, ESSENTIAL.**TARTAR v. TARTARIC ACID.**

TARTAR, CREAM OF, Potassium hydrogen tartrate, v. TARTARIC ACID.

TARTAR EMETIC. Examination of the alleged antimonious hydroxides prepared from barium antimonyl tartrate and sulphuric acid, from tartar emetic and hydrochloric acid, and by the action of alkali carbonates or hydroxides on antimony trichloride (C. Lea and J. K. Wood, T. 1923, 123, 259), and of specimens of hydrated antimony pentoxide prepared in various ways (G. Jander and A. Simon, Zeitsch. anorg. Chem. 1923, 127, 68; Chem. Soc. Abstr. 1924, 124, 772), shows that no stable hydroxide exists in either case. *Potassium antimony tartrate v. ANTIMONY.*

For the electrical conductivity of potassium antimonyl tartrate (*tartar emetic*), see Svanberg (Chem. Soc. Abstr. 1920, ii. 73).

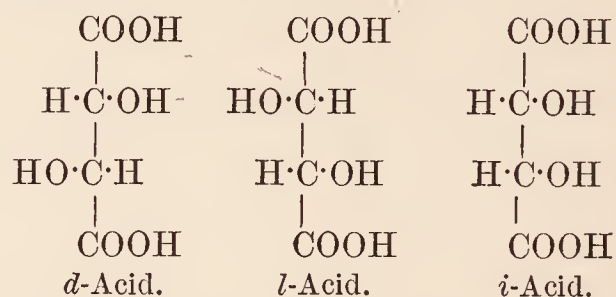
TARTARIC ACID, Dihydroxysuccinic acid (*Acide tartarique; Weinsäure, Weinsteinsäure, Tartarsäure*), $C_4H_6O_4$.

The existence of the acid potassium salt of this acid in the deposit from fermented grape-juice was known to the Greeks and Romans, and the term 'tartarum' was applied to the deposit by Paracelsus, but it was generally considered to be an acid and to contain no base, although an alkali was known to be present in the ash. The production of an alkali by boiling tartar with lime was noticed by Kunkel in 1677, but the acid was not isolated until 1769, when Scheele obtained it by boiling tartar with chalk and decomposing the product with sulphuric acid.

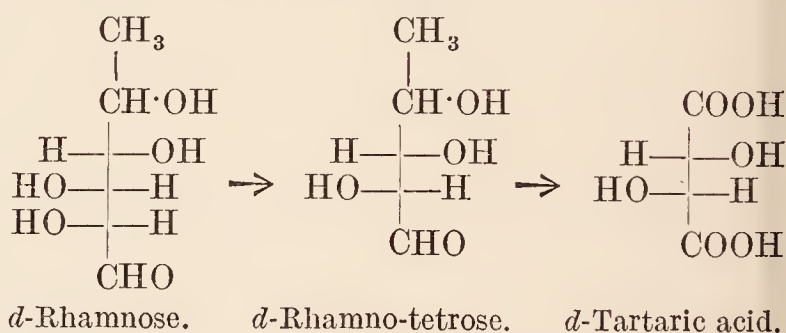
The distinction between cream of tartar and the normal potassium tartrate was first clearly established by Cavendish.

Tartaric acid contains two asymmetric carbon atoms and hence exists in four modifications, viz.: *d*-tartaric acid and *l*-tartaric acid which rotate the plane of polarised light to the

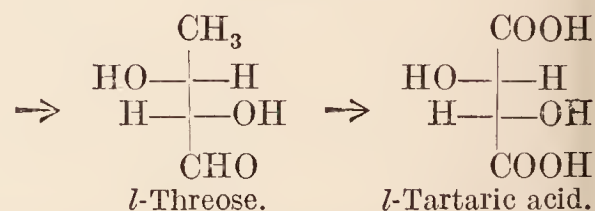
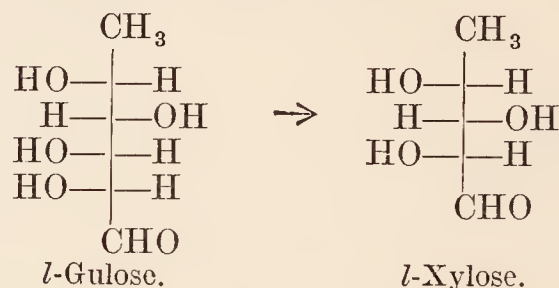
right and left respectively; *r*-tartaric acid or racemic acid which is optically inactive, being a racemic mixture of the above two acids; *i*-tartaric acid or *mesotartaric acid* which is also optically inactive, as the lower half of the molecule is the mirror image of the upper half. Racemic acid is said to be 'externally compensated' and *mesotartaric acid* 'internally compensated.' The configurations of *d*-, *l*-, and *i*-tartaric acids are shown below:—



The relative configuration of *d*- and *l*-tartaric acids to the sugars was determined by Fischer (Ber. 1896, 29, 1377). The configuration of the *d*-acid was determined by converting rhamnose into rhamno-tetrose by the Wohl degradation and oxidising the methyl tetrose to *d*-tartaric acid with nitric acid.



Similarly the configuration of the *l*-acid was determined from *l*-gulose.



Physico-chemical data.—The following table compares some of the constants of the four acids:—

—	M.p.	Sp.gr.	Mol. of water of cryst.	No. of grams dissolved by 100 grams H_2O	Affinity constant
<i>d</i> -Tartaric acid	168° – 170°	1.755	—	132.2	0.097
<i>l</i> -Tartaric acid	168° – 170°	1.754	—	132.2	0.097
<i>r</i> -Tartaric acid	205° – 206°	1.697	1 H_2O	17.07	0.097
<i>i</i> -Tartaric acid	140°	1.666	1 H_2O	125.3	0.96

The specific gravity of solutions of *d*-tartaric and racemic acids of equal concentration are in

close agreement up to concentrations of 10 p.c. Between concentrations of 10 p.c. and 14 p.c. the solution of racemic acid has a smaller specific volume than that of one of tartaric acid of the same concentration, as shown in the following table:—

Percentage of acid in solution	Sp.gr. of tartaric acid solution	Sp. gr. of racemic acid solution	Sp. vol. of tartaric acid solution (d_1)	Sp. vol. of racemic acid solution (d_2)	$d_1 - d_2$
10·666	1·04950	1·04969	0·95283	0·95266	0·00017
14·018	1·06600	1·06623	0·93809	0·93788	0·00021

The specific gravities of 4 p.c. solutions of *d*- and *l*-tartaric acids are 1·01770 and 1·01767 respectively. On mixing the two solutions to obtain racemic acid the values obtained in two experiments were 1·01769 and 1·01766. Hence there is no change in specific gravity. All these values are compared with water at 4° and reduced to vacuum (Marchlewski, Ber. 1892, 25, 1556). According to Jahn (Wiedemann's Annalen, 1891, 43, 306) when *d*- and *l*-tartaric acids are mixed to give racemic acid, no heat is evolved. Also the heat of neutralisation of *d*- and *l*-tartaric acids by optically active bases is the same. The following data are given by Berthelot (Compt. rend. 1891, 112, 827). When solutions of the sodium salts of *d*- or *l*-tartaric acids are mixed with calcium chloride solution, at first heat is developed, but no precipitate is formed. After a few minutes a precipitate separates with a further development of heat. The values for *d*-tartaric acid are +0·98 Cal. and +2·68 Cals., and for *l*-tartaric acid +0·92 Cal. and +2·61 Cals. When the sodium salts of *d*- and *l*-tartaric acid are mixed to give sodium racemate, there is no development of heat. The heats of neutralisation of the four tartaric acids by sodium hydroxide are practically identical under similar conditions of temperature and concentration; viz. +12·7 Cals. per equivalent. The rates of diffusion of *d*- and *l*-tartaric acids are the same (Marchlewski, Ber. 1893, 26, 983). For relation between the optical activity and absorption spectra of the tartaric acids, *v.* Stewart, Chem. Soc. Trans. 1907, 1037.

For heat of combustion Berner found tartaric acid in the *meso*-form gave 623·2 Cals. (kilo. cal. per grm. mol.); in the *d*-form 621·8 Cals. Correcting for the difference in the heat of solution, the difference is 2·6 Cals. *r*-Tartaric acid gave 0·5 Cal. more heat than the *d*-isomeride. Ossipoff (Compt. rend. 1889, 109, 475) found 619·5 and 618·5.

Physiological action.—According to Chabrière (Compt. rend. 1893, 116, 1410) the order of toxicity of the tartaric acids as determined by experiments on guinea pigs is *l*-tartaric acid, *d*-tartaric acid, racemic acid, and *mesotartaric* acid, the *l*-acid being twice as poisonous as the *d*-acid (*cf.* Salant and Smith, Amer. J. Physiol. 1914, 35, 239). Karczag examined the effect of the four acids on the cardio-inhibitory and vaso-motor centres and on the isolated cardiac ventricle by intravenous injection (Zeitsch. Biol. 1909, 53, 218). On the cardio-

inhibitory and vaso-motor centres, *l*-tartaric acid is the most reactive and *d*-tartaric acid the least, racemic and *mesotartaric* acids occupying intermediate positions. *Mesotartaric* acid has the least action on the isolated cardiac ventricle. When dogs are fed with *d*- or *l*-tartaric acid or with racemic acid, the acids pass unchanged into the urine. Hence there is no evidence that *d*- or *l*-tartaric acids are consumed at different rates in the body (Neuberg and Saneyoshi, Biochem. Zeitsch. 1911, 36, 32). According to Biron, *l*-tartaric and *mesotartaric* acids are most completely oxidised in the organism of a dog, the *d*-acid much less so, and racemic acid least of all. Hence racemic acid is not resolved into *d*- and *l*-tartaric acids in its passage through the organism (Zeitsch. physiol. Chem. 1898, 25, 283).

More carbon dioxide is evolved in the earlier stages of the reaction between yeast and *d*-tartaric acid than is the case when *l*-tartaric acid is used. Racemic acid occupies an intermediate position, while *mesotartaric* acid acts similarly to *d*-tartaric acid (Karczag, Biochem. Zeitsch. 1912, 38, 516).

For the physiological action of tartaric acid, *see* Hara (Chem. Soc. Abstr. 1921, i. 478).

Separation of the tartaric acids.—Holleman (Rec. trav. chim. 1898, 17, 66) devised the following method for the separation of *d*-tartaric acid, racemic acid, and *mesotartaric* acid. The aqueous solution of the free acids is evaporated on the water-bath until crystallisation commences and the liquid is then left for 24 hours in a cool place. The racemic acid separates quantitatively and the crystals are drained, dried, and weighed. The mother-liquor is diluted to 20 c.c., and 10 c.c. of this are neutralised with potassium hydroxide and the other 10 c.c. are added and the liquid is left overnight, when potassium hydrogen *d*-tartrate separates out and is filtered, washed with a very little water, dried and weighed. The filtrate is neutralised with ammonia, made slightly acid with acetic acid, boiled and treated with calcium chloride solution. After leaving for a further 24 hours the calcium *mesotartrate*, which has separated, is filtered, dried, and weighed.

d-TARTARIC ACID.

d-Tartaric acid has been obtained together with racemic acid by the oxidation of saccharic acid, dextrose, cane-sugar, milk-sugar, starch, gum arabic and sorbin with nitric acid (Des-saignes, Annalen, Suppl. 2, 242; Horsemann, J. 1863, 38; Kiliani, Annalen, 1880, 205, 175). If 100 parts of starch are mixed with 150 parts of water and saccharified, and to the product 25 parts concentrated sulphuric acid, 120 parts of nitric acid (D 1·4), and some mercury are added, a yield of 60 p.c. tartaric acid and 10 p.c. saccharic acid may be obtained (Diamalt, Akt. Ges.; Eng. Pat. 108494; Chem. Soc. Abstr. 1920, i. 708). It can also be obtained by the resolution of racemic acid and its salts into their optical antipodes (*v. infra*). For asymmetric synthesis from *d*-bornyl fumarate by the action of potassium permanganate, *v.* McKenzie and Wren, Chem. Soc. Trans. 1907, 1215. According to Zinno tartaric acid can be synthesised by the following methods: (i.) by oxidising succinic

acid in cold concentrated aqueous solution with hydrogen peroxide; (ii.) by oxidising calcium succinate with calcium hypochlorite; (iii.) by treating glyceric acid of 26°B. with a solution of potassium hydroxide of sp.gr. not greater than 1.134 at 15°, and finally with carbon dioxide under a pressure of 3 atmos., whereby cream of tartar is produced; (iv.) by heating *l*-malic acid with hydrogen peroxide at 120°; if an ethereal solution of *l*-malic acid is used, a mixture of *d*-tartaric and racemic acids is obtained (Mon. Sci. 1902, 16, 493; L'Orosi, 1902, 25, 293).

Occurrence. Tartaric acid occurs in nature in the free state, or, more often, as the acid potassium salt and to a small extent as the calcium salt in association with oxalic, malic, citric, and probably racemic acid, in tamarinds, mulberries, sorrel, cucumbers, and many other plants. It occurs in large quantity in the juice of the grape, which furnishes practically all that is found in commerce. According to Winter (Zeitsch. ver. Rübenzucker Ind. 1888, 38, 380) it does not exist in the juice from the sugar-cane, but it is found in the precipitated calcium salts obtained in the treatment of beet juice (Lippmann, Ber. 1894, 24, 3299). Metzger states that tartaric acid is present in oak wood (Bied. Zentr. 1897, 26, 678). When tartaric acid is added to a solution containing potassium malate, succinate, pectinate, acetate, hydrogen sulphate, or hydrogen phosphate or a mixture of these salts, potassium hydrogen tartrate is always precipitated. Hence Carpené concludes that tartaric acid cannot exist in the free state in wines in the presence of these salts (Selmi, 1894, 4, 13).

A possible explanation of the occurrence of tartaric acid in nature has been given by Genvresse (Compt. rend. 1892, 114, 555). By the action of nascent hydrogen glyoxylic acid is converted into racemic acid. The former acid occurs in nature in unripe grapes, gooseberries, &c., and it may be that the tartaric acid is produced from the glyoxylic acid in an analogous manner.

When the grape juice ferments, the potassium hydrogen tartrate is gradually deposited, on account of its less solubility in the alcohol produced, partly as a crystalline crust on the sides of the vat and partly with the 'lees' which consists of yeast and the various suspended matters of the must. The crust is known as 'argol,' and when recrystallised produces 'tartar,' which by further crystallisation is converted into 'cream of tartar,' technically known as 'cream.'

The quality of lees, argol, and tartar varies enormously. Superior argols are equal to tartar, while inferior varieties are little better than lees. The tartaric acid in argols varies from 40 to 70 p.c., and that in lees averages about 25 p.c., but varies within wide limits. Lees from 'plastered wines,' i.e. from those in which baked gypsum or 'yesso' has been trodden with the grapes, as in Spain, Cyprus, and the Greek Islands, the Marsala district of Sicily, and the South of France, contain very little tartar, the acid being mostly present as the calcium salt.

The wine districts of Southern France and Algeria are the world's largest sources of cream of tartar, the average annual production of argols being 10,000 tons. Of this quantity

(which contains 75 p.c. of cream of tartar) some 5200 tons are exported to the United States, 2000 to England, 800 to Germany, and 2000 are consumed in France. The 18 cream of tartar factories in France had an annual production before the war of 6000 tons, but now produce only 2000 tons. In addition to the argol production some 15,000 tons of wine lees containing from 18 to 20 p.c. of cream of tartar are also available annually. The principal centre of the cream-of-tartar trade in France is Montpellier (U.S. Com. Rep. Jan. 18, 1923; J. Soc. Chem. Ind. 1923, 214).

The best class of coloured tartars consist of nearly pure potassium hydrogen tartrate. That of Messina usually contains 76 p.c. of tartaric acid, 1½–3½ p.c. of which is present as the calcium salt, whilst that from St. Antimo contains 74–75 p.c., of which the calcium salt constitutes 3–4½ p.c. Vinaccie tartar, which is obtained from the skins and solid matters of grapes, contains about 70–73 p.c. of tartaric acid, 5–7 p.c. being calcium salt. Occasionally much greater quantities of calcium tartrate are found in crude tartar. The table (p. 681) shows the composition of tartars and lees from different localities (Warington, J. Soc. Arts. 1876, 370).

The following table shows the general composition of lees (Warington, *l.c.*) :—

—	Tartaric acid as		Total tartaric acid
	Potassium hydrogen tartrate	Calcium tartrate	
Italian (33 samples)	24.10	6.1	30.2
Greek (14 samples).	19.90	11.8	31.7
French (9 samples).	17.30	6.0	23.3
" (30 samples).	5.30	20.5	25.8
Yellow Spanish { (59 samples) }	8.70	18.2	26.9
Red Spanish (17 samples) . }	8.80	17.4	26.2

The lees often contain calcium carbonate; also Spanish earth (a native aluminium magnesium silicate used in fining wine); gypsum when the wine has been plastered; a resin when obtained from the Greek Islands. The vegetable matter contains considerable quantities of nitrogen. The lees are used for the manufacture of tartaric acid, either in the moist condition or after being dried. The moist pasty lees are removed from tuns into sacks and pressed. They contain varying amounts of potassium hydrogen tartrate and calcium tartrate with some alcohol and higher esters. They are mixed with water and distilled, the distillate yielding the so-called Lager brandy and wine oil or Cognac oil. The residue, which is used for the manufacture of tartaric acid, contains from 1.8 p.c. of the acid. Lees containing a higher percentage of tartaric acid, which only occurs after the first stage of the fermentation, are well pressed and dried, usually by the heat of the sun, and sold as dried wine lees. For an account of the tartar industry in Italy, see Molinari, G. Chim. Ind. ed. App. 1922; J. Soc. Chem. Ind. 1922, 41, 159 R.

Production of Cream of Tartar in France.—The wine districts of southern and southwestern France and Algeria are the largest sources of supply of cream of tartar in the world.

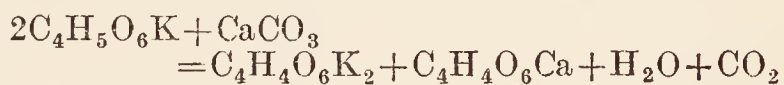
It is estimated that Southern France and North Africa produce on an average 10,000 tons of argols per annum. These crystals contain 75 p.c. of cream of tartar. Sometimes the scraping of the casks is deferred until two or three years' precipitation has accumulated. In years when the price of wine is low, the growers scrape their casks in order to supplement their income by the sale of the argols, and accordingly in such years as much as 12,000 tons of argols may be offered; in years when the price of wine is such that growers do not feel the need of funds, they are apt to leave their casks unscraped, and the offering of argols may be as low as 8000 tons. The higher the alcoholic content of wine the lower is the precipitation of argols; so that the ordinary red wines with nine degrees of alcohol give more tartar than the high-grade wines with

12°–20° of alcohol. Of the average figure of 10,000 tons it is estimated that some 4000 tons find their way to two large American firms, whose importing headquarters are at New York City. Of the remaining 6000 tons some 1200 go to independent buyers in the United States, 2000 tons come to England, 2000 tons are used in France, and 800 tons go to Germany. Many of the largest American baking-powder companies do not buy cream of tartar, as they manufacture alum powders. Even the oldest American baking-powder companies are now adding tartaric acid to their formulas to replace a part of the cream of tartar formerly used. The English baking-powder companies employ a higher proportion of tartaric acid than has been used in the United States until recently. According to a report by the United States Consul at

	Messina tartar	St. Antimo tartar	French lees (plastered)	Spanish lees (plastered)	Spanish lees (unplastered)
Tartaric acid as acid tartrate .	74·05	69·34	4·48	5·27	22·66
Tartaric acid as neutral tartrates	2·60	4·66	21·34	19·13	11·67
Tartaric anhydride	67·408	65·120	22·721	21·472	30·210
Sand	0·140	0·425	4·600	4·900	} 4·730
Silica	0·055	0·130	2·130	1·960	
Ferric oxide	0·053	0·086	0·394	0·351	0·214
Alumina	0·021	0·092	0·844	0·832	0·578
Phosphoric anhydride	0·041	0·068	0·527	0·486	0·569
Lime	1·081	1·778	10·567	10·600	4·514
Magnesia	0·025	0·041	0·327	0·363	0·209
Potash	23·236	21·773	1·868	2·123	7·115
Soda	—	—	0·100	0·060	—
Sulphuric anhydride	—	—	4·566	5·729	—
Carbon dioxide	—	—	0·435	0·388	—
Chlorine	—	—	0·040	0·042	—
Combined water	5·688	6·396	5·904	5·552	4·159
Water at 100°, with vegetable and undetermined matter }	2·252	4·091	—	—	—
Water at 100°	—	—	11·305	10·694	9·750
Vegetable matter	—	—	33·672	34·448	37·952
	100·000	100·000	100·000	100·000	100·000

Marseilles, France has eighteen cream of tartar factories, located chiefly in Marseilles, Montpellier, Beziers, Aubais, St. Thibéry, and Bordeaux. Prior to the war these factories exported something like 6000 tons of cream of tartar per annum, but this figure has now shrunk to approximately 2000 tons. The sales are made largely in Australia, Canada, England, and Japan. In addition to the argol production there are available in the south of France and Algeria each year some 15,000 tons of wine lees taken from the bottom of wine casks, containing from 18 to 20 p.c. of cream of tartar. About 3000 tons of these have been worked up in France, but an additional 4000 tons are now to be used in a factory at Montpellier. About 2000 tons of wine lees are also exported to Germany and the remainder discarded (Journal of the Royal Society of Arts, August 24, 1923; Pharm. Journ. 1923, vol. iii. p. 281).

Preparation and manufacture. Scheele's process for preparing the acid consisted in merely neutralising the solution of the tartar with chalk, and decomposing the precipitated tartar with sulphuric acid. By this process, however, only half the acid was extracted, the rest remaining in solution as potassium tartrate:—



The first improvement on this process consisted in the replacement of chalk by lime, which produced a larger yield although a portion of the calcium tartrate was retained in solution by the potassium hydroxide produced. Lowitz next suggested the precipitation of the residual tartrate from the solution, after the treatment with chalk, by addition of calcium chloride (Aitkin's Diet. of Chemistry, 1807, ii. 405). This was in turn superseded by a process attributed

to Desfosses, and consisting in the replacement of the calcium chloride by the precipitated calcium sulphate obtained by treatment of calcium tartrate with sulphuric acid.

The methods in use vary according to the nature of the crude material. A suitable mode of procedure in the case of an argol is to mix the powdered argol with water, add hydrochloric acid and boil (4–5 cub. metres of water and 110–120 kilos. of crude hydrochloric acid of 20°–22°B. with 500 kilos. of argol). The solution is nearly neutralised with milk of lime, whereby calcium tartrate is precipitated and potassium tartrate and calcium chloride remain in solution. The potassium tartrate is decomposed either by boiling with a sufficient quantity of calcium sulphate or by adding calcium chloride solution, an excess of the precipitant being avoided in either case. The small amount of potassium hydrogen tartrate purposely left in the liquid, when treating the latter with milk of lime, is decomposed with pure precipitated calcium carbonate. The object of not adding sufficient milk of lime to neutralise the solution is to avoid the precipitation of iron oxide and alumina. The liquid must still remain slightly acid after the addition of the calcium carbonate. After cooling to about 40°C. the liquid is filtered with the aid of a suction pump and the residue washed with water. The calcium tartrate is then mixed with water and decomposed with dilute sulphuric acid, a portion of the solution being tested at intervals to ascertain when sufficient acid has been added; the reagent employed is calcium chloride, which gives no precipitate with the calcium sulphate contained in the solution, but precipitates the free acid.

The gypsum resulting from the decomposition is washed on a vacuum filter, and the liquors are evaporated in steam-heated leaden pans, or in vacuum pans. After partial concentration the liquor is run off from the gypsum which has deposited on the sides of the pan, and is concentrated to the crystallising-point when it is run into a tub and continuously agitated by a mechanical stirrer to produce a granular 'salt.' This system of crystallisation separates the salt in about a fifth of the time required for crystallisation by standing. The mother-liquor from the 'salt' is concentrated and a second and third crop of crystals are obtained by 'granulation' as above; the residual dark-coloured impure solution is known as 'old liquor.' The granular salt is re-dissolved, heated with animal charcoal which has been freed from calcium phosphate by digestion with hydrochloric acid; the solution is filtered, concentrated, and crystallised in cylindrical leaden pans about 2 feet deep. Tartaric acid thus prepared always contains lead. The crystallisation is assisted by the addition of sulphuric acid, in which the acid is less soluble than in water (*v. infra*).

The mother-liquors are diluted and precipitated with milk of lime, and thus produce a further quantity of calcium tartrate, which is worked up as above. It is found, however, that the iron, alumina, and phosphoric acid introduced in the tartar, charcoal, whiting, &c., gradually accumulate in the liquors, and greatly reduce their power of crystallising so that con-

tinuously more and more sulphuric acid must be added to induce crystallisation. According to Carles (Bull. Soc. chim. 1910, [iv.] 7, 326) the iron may be removed by precipitation with potassium ferrocyanide and filtration, when crystallisation is much facilitated. The 'old liquor' finally becomes thick and yields no tartaric acid, although a considerable quantity remains in solution, together with a large amount of decomposition products, principally due to the action of the sulphuric acid. A process has been patented for obtaining the potassium salts which are present in the calcium tartrate mother-liquors (Alberti, Fr. Pat. 402925; J. Soc. Chem. Ind. 1909, 1313).

The manufacture of tartaric acid from lees and low argols may be carried out by Scheurer-Kestner's process which consists in dissolving the lees, &c., in hydrochloric acid, which separates it from most of the organic impurities and colouring matters. The solution is precipitated by whiting or lime and treated as above (Scheurer-Kestner, Wurtz, Dict. of Chem. iii. 263). This extraction, however, is incomplete. If the filtration of the lees is attempted, the pores of the filter become clogged and even under a pressure of four or five atmospheres no liquid will pass through. Dietrich and Schnitzer overcame this difficulty by heating the lees under a pressure of 4 or 5 atmospheres for 6 hours, whereby the albuminoid substances are coagulated. Wet lees, when thus treated, can be readily filtered. Dried lees or argols are crushed, stirred in a tank with water, and heated by steam for half an hour, and then transferred to the pressure boiler. The lees are then treated with the requisite quantity of hydrochloric acid (21°–22°B.), filtered, pressed, and washed. The tartaric acid is precipitated with lime and calcium carbonate and the remaining operations are the same as in the treatment of argols with the exception that there is no need to add calcium chloride or sulphate.

Many modifications of the above processes have been patented. J. B. Lawes & Co. mix chalk and lime with a 27–35 p.c. solution of anhydrous calcium chloride and stir the tartar into the mixture. The amount of calcium chloride used should be greater than that of the chalk and the lime, and after the tartar has been added the chalk and lime should be in slight excess. After settling, the liquid is again treated with the calcium chloride mixture. The solid residue is decomposed with sulphuric acid in the usual manner (Eng. Pat. 11694; J. Soc. Chem. Ind. 1910, 1488). Schmitz and Toenges boil argols or crude tartars with slight excess of alkali carbonate and treat the warm lye with sodium hypochlorite until the colour has changed from brown to light yellow. The solution is neutralised with acetic or hydrochloric acid and the tartaric acid is precipitated with calcium chloride. The calcium tartrate thus obtained is boiled with alkali carbonate and treated as above. If cream of tartar is required, after boiling the calcium tartrate with potassium carbonate, the calcium carbonate is filtered off and a suitable acid added to precipitate the cream of tartar (Eng. Pat. 21178; *ibid.* 1897, 799). Another process, whereby a saving of 50 p.c. in reagents is claimed, consists in dividing the crude material into two parts and treating

one portion with alkali and the other with acid. To the acid portion is added an amount of oxalic acid equivalent to the calcium salts present and to the alkali portion potassium chloride or other potassium salt, so that on mixing the two solutions all the tartaric acid is precipitated as potassium hydrogen tartrate and all the calcium salts as calcium oxalate. The precipitate, after being filtered, is treated with hot water containing a small quantity of oxalic acid and on filtering and cooling the solution, potassium hydrogen tartrate separates out. The oxalic acid can be recovered and used again (Cantoni, Chautemo et Cie. et Degrange, Fr. Pat. 426714; *ibid.* 1911, 956). Another method, having the same object in view, is that of Moszczenski (U.S. Pat. 1000433; *ibid.* 1911, 1115). The crude material is made into a paste with water, and lime is added, whereby potassium tartrate is formed in solution, leaving calcium tartrate in the residue. The liquid is filtered off and tartaric acid obtained from the residue by the addition of sulphuric acid. On mixing the two solutions, potassium hydrogen tartrate is precipitated. Perigny and Mazet treat the crude material electrolytically and by the use of suitable anodes, obtain metallic tartrates. The yield is improved by esterifying one or both of the alcoholic hydroxyl groups with boric or antimonious acid and subsequently hydrolysing the product (Fr. Pat. 382824; *ibid.* 1908, 296, 470).

Methods for the treatment of lees have been patented by Auzies, Secheyron and Subra (Fr. Pat. 429008; *ibid.* 1911, 1253), and by Martignier and Montpellier (Eng. Pat. 20078; *ibid.* 1891, 253). The former add sulphuric acid to the lees and sufficient hot water to dissolve the potassium sulphate and tartaric acid thus formed. On cooling the potassium sulphate separates out and the tartaric acid may be obtained from the mother-liquors by concentration and crystallisation. If much pectic substance be present the tartaric acid is best obtained by dialysis. The latter neutralise the lees and add an excess of a saturated solution of potassium sulphate, calcium sulphate being precipitated, and potassium tartrate going into solution. The filtered solution is decolorised with animal charcoal and sulphuric acid added to precipitate the potassium hydrogen tartrate.

If grape marcs form the crude material, they are usually only pressed or extracted with hot water, since after this treatment they can be sold as fodder for cattle, whereas if acid has been used, they become valueless for this purpose (Janson, Chem. Ind. 1909, 32, 719). Most processes for utilising grape marcs as a source of tartaric acid also aim at recovering the alcohol they contain. Salat extracts the marcs with water or with a liquid which has previously been obtained in the process. Sufficient sulphuric acid is added to the extract to decompose all calcium tartrate, and enough oxalic acid to dissolve all the potassium hydrogen tartrate. After 6 hours the alcohol is distilled off and the residual liquid is treated, while hot, with enough potassium sulphate to convert all the tartaric acid into potassium hydrogen tartrate and immediately afterwards with sufficient lime or chalk to neutralise the sulphuric and oxalic acids. After standing for 30 minutes the liquid is filtered and

potassium hydrogen tartrate separates from the filtrate on cooling (Fr. Pat. 421730; *ibid.* 1911, 441). Barbet lixiviates the marcs in a battery with water made alkaline with sodium carbonate. To the extract is added an amount of sulphuric acid exactly equivalent to the sodium carbonate used. After a few days the liquid is filtered and the alcohol distilled off. The cream of tartar is then obtained as such by evaporation or as calcium tartrate by precipitation with calcium chloride (Fr. Pat. 379038; *ibid.* 1907, 1211). Ciapetti charges a series of diffusion vessels with the marcs, drives off the alcohol by steam and then acts on them with an aqueous solution of sulphurous acid under pressure. This treatment decolorises the solution and gives potassium hydrogen sulphite and tartaric acid in solution. After this solution has passed through the series of vessels, it is heated to 80°, whereby sulphur dioxide is expelled and cream of tartar is precipitated (Fr. Pat. 330951; *ibid.* 1903, 1099). Jude dissolves out the tartaric acid by the addition of an acid to the marcs and treats the filtrate with a potassium salt, such as the chloride, and a carbonate in quick succession so as to obtain a precipitate rich in potassium hydrogen tartrate (Fr. Pat. 402999; *ibid.* 1909, 1326; cf. Carles, Fr. Pat. 365034; *ibid.* 1906, 952).

A preliminary treatment of the crude material to render the colouring matters which are present insoluble, forms the subject of several patents. The crude lye may be boiled for 45 minutes after treatment with formalin (*ibid.* 1909, 913); if the proportion of albuminous material in the lye is low, blood, white of egg, casein or glue, &c., is added and then formalin and the substance taken to dryness at 140° (Garin and David, Fr. Pat. 374276; *ibid.* 1908, 712). Crude tartrates are treated with 1-2 p.c. of formalin or trioxymethylene and dried; the liquids obtained subsequently by extraction have very little colour (Garin, Annemasse and David, Fr. Pat. 8375; *ibid.* 1907, 778). Faucheux and Boissière submit the crude material to a slight roasting by means of hot gases from a furnace, whereby all organic matter other than tartrates is decomposed and the iron and aluminium compounds which are present, are rendered insoluble (Fr. Pat. 338735; *ibid.* 1904, 680). Vigneaux adds acid to the crude material and then zinc or some other metal to remove the excess of the acid, the hydrogen evolved decolorising the liquid. When the acid has been neutralised, potassium hydrogen tartrate is first deposited and finally calcium tartrate (Fr. Pat. 430883; Eng. Pat. 11558; *ibid.* 1911, 1382).

Fermaud extracts the crude substance with a hot solution of aluminium chloride or nitrate and claims thereby to get a purer product (D. R. P. 247452; *ibid.* 1912, 773). Special boilers for extracting the crude material have been patented by Roux (Eng. Pat. 7363; Fr. Pat. 328713; *ibid.* 1903, 1014) and Chauvin (Fr. Pat. 385103; *ibid.* 1908, 591). Cornette and Faucheux have patented a process for centrifugating out the potassium hydrogen tartrate after extracting the crude material with water (Eng. Pat. 5759; Fr. Pat. 435915; *ibid.* 1912, 386, 1125).

Other sources of tartaric acid than the grape have been proposed. Brehier and Talbot treat cellulose, saccharic or amylaceous substances with alkaline permanganate in the presence of chlorine. The nascent oxygen reacts on the glucose bodies and a tartaric acid liquor is produced from which the tartaric acid may be obtained by the usual methods (Eng. Pat. 3240; *ibid.* 1891, 751). Ellis treats a solution of a saccharic substance electrolytically and by anodic oxidation in the presence of substances yielding insoluble compounds with tartaric acid, obtains insoluble tartrates which are immediately removed from the field of oxidation (U.S. Pat. 789269; *ibid.* 1905, 635).

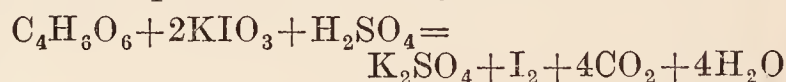
Tartaric acid is formed by oxidising carbohydrates with sulphuric acid and nitric acid in presence of a catalyst, *e.g.* mercury. 100 parts of starch are mixed with 150 parts of water and 3 parts of sulphuric acid and saccharified. Concentrated sulphuric acid (25 parts), nitric acid (D. 1.4, 120 parts) and mercury are then added and the mixture is maintained at 100°, a further 200 parts of nitric acid being gradually introduced. At the end of the operation the nitric acid is evaporated, and after diluting the residual liquor with water, the mercury is precipitated by hydrogen sulphide, and the sulphuric acid, and traces of oxalic acid, by lime or baryta, and the tartaric acid separated from the filtrate, after concentration, as potassium hydrogen tartrate. The yield is 60 p.c. tartrate, and about 10 p.c. saccharate (Diamalt, Akt. Ges. Eng. Pat. 108494).

The crude tartrates so obtained may be further purified by one of the following methods. Scarlata decomposes them with hydrofluosilicic acid yielding a residue of potassium fluosilicate while tartaric acid and calcium fluosilicate go into solution. After filtering, a slight excess of sulphuric acid is added to decompose the calcium fluosilicate and the precipitate of calcium sulphate having been removed, the tartaric acid is crystallised out (Mon. Sci. 1899, 783). Another method is to convert the crude tartrate into an alkali salt and add sulphuric acid. The filtered liquid is treated with aluminium sulphate in quantity sufficient to form an alum, and the latter is removed by evaporation and crystallisation. The tartaric acid is recovered from the mother-liquors (Sir J. McDougall and F. L. McDougall, Eng. Pat. 4613; U.S. Pat. 898253; J. Soc. Chem. Ind. 1907, 1215). To obtain colourless cream of tartar, crude calcium tartrate is decomposed with sulphuric acid which has been freed from arsenic with sulphuretted hydrogen. After filtration the liquid is treated with purified animal charcoal and a small quantity of sodium thiosulphate, which prevents any iron or aluminium compounds being precipitated subsequently. After agitation the solution is again filtered and potassium carbonate added to precipitate the potassium hydrogen tartrate (Condouris and Tassopoulos, Fr. Pat. 366058; *ibid.* 1906, 1003; Tassopoulos, Eng. Pat. 16047; *ibid.* 1908, 876; *cf.* also Martignier, Eng. Pat. 27328; *ibid.* 1899, 1154).

Analysis of Crude Tartar and Argol.—Six grms. of material containing more than 45 p.c. of tartaric acid or 12 grms. of that containing less is dissolved in 18 c.c. of hydrochloric acid

(sp.gr. 1.1), and the liquid is made up to 200 c.c. in a graduated flask. 100 c.c. of the solution, filtered through a dry paper, is boiled for 20 mins. with 10 c.c. of potassium carbonate solution (sp.gr. 1.48), and diluted to 200 c.c. in a graduated flask. 100 c.c. of the clear liquid is treated with 3 c.c. of hydrochloric acid (sp.gr. 1.1), and the mixture is digested for 15 mins. on the water-bath, made just alkaline to phenolphthalein with 10 p.c. potassium hydroxide solution, and evaporated to a volume of 15 c.c., 25 c.c. of hot water is added, followed by 5 grms. of solid potassium chloride, and 5 c.c. of dilute acetic acid added, drop by drop, with constant stirring. After 5 mins. on the water-bath the whole is set aside overnight. The precipitated potassium bitartrate is collected on a vacuum filter, washed with 20 p.c. potassium chloride solution previously saturated with the bitartrate, and dissolved in 200 c.c. of water. The solution is titrated with sodium hydroxide, using phenolphthalein as indicator. With very impure materials the solution may be too dark-coloured to titrate; in this case the hydrochloric acid solution of the original substance must be treated with 0.5 gm. of decolorising carbon before dilution to 200 c.c. For exact work allowance must be made for the bulk of the precipitate in the graduated flasks. The method has been tested in Fresenius' laboratory and found to give results agreeing very closely with those obtained by the older process involving precipitation with alcohol and the use of litmus paper as indicator, the new process is also simpler and cheaper (Zeitsch. anal. Chem. 1923, 63, 111; J. Soc. Chem. Ind. 1923, 42, 1241 A).

Determination of tartaric acid by oxidation with potassium iodate and sulphuric acid.—The reaction proceeds according to the equation



1 gm. of potassium iodate with concentrated sulphuric acid is placed in a flask, a weighed quantity of about 0.3 gm. of tartaric acid is added, and the mixture is heated on a sand-bath until the greater part of the iodine has been expelled; this requires about 30 minutes. The mixture is then cooled, diluted with water, boiled to expel the remaining traces of iodine, again cooled, diluted to a definite volume, and the excess of iodate is determined in an aliquot portion of the solution by titration with thio-sulphate solution after the addition of potassium iodide. The method may be applied to tartrates, and, if desired, the tartaric acid may be precipitated as lead tartrate by treatment with lead acetate in acetic acid solution; the lead tartrate is collected, washed with hot water, and then oxidised as described (R. Strebing and J. Wolfram, Oesterr. Chem. Zeit. 1923, 26, 156; J. Soc. Chem. Ind. 1924, 43, B. 74).

Properties.—Tartaric acid crystallises in large anhydrous monoclinic prisms having sp.gr. 1.755 (Walden, Ber. 1896, 29, 1701) and m.p. 168°–170° (Bischoff and Walden, *ibid.* 1889, 22, 1814). For its crystalline structure, *v.* Astbury, Proc. Roy. Soc. 1923, [A.] 102, 506. The crystals become luminous in the dark when rubbed. They often contain traces of lead owing to their having been crystallised in lead pans. The solubility of tartaric acid in water is given

in the following table, the values being the same for *d*- and *l*-tartaric acids (Leide, Zeitsch. anal. Chem. 1883, 22, 269). The second column gives the number of parts of tartaric acid dissolved by 100 parts of water.

Temp.	Solubility	Temp.	Solubility
0°	115·04	55°	205·83
5°	120·0	60°	217·55
10°	125·72	65°	230·16
15°	132·20	70°	243·66
20°	139·44	75°	258·05
25°	147·44	80°	273·33
30°	156·20	85°	289·50
35°	165·72	90°	306·56
40°	176·0	95°	324·51
45°	185·06	100°	343·53
50°	195·0		

100 parts of 90 p.c. alcohol dissolve 29·146 parts of tartaric acid, whilst 100 parts of absolute alcohol at that temperature dissolve 20·385 parts (Bourgoin, Bull. Soc. chim. 1878, [ii.] 29, 244; cf. Schiff, Annalen, 1860, 113, 189). 100 parts of ether dissolve 0·393 parts at 15° (Bourgoin, *l.c.*). A solution of tartaric acid saturated at 15° contains 57·9 parts of the acid (Gerlach, J. 1859, 44) or 57·75 parts (Maisch, *ibid.* 1865, 392). The following table of specific gravities contains Gerlach's results (cf. Maisch, *l.c.*: Schiff, *l.c.*; Marchlweski, Ber. 1892, 25, 1560; Přibram and Glücksmann, Monatsh. 1898, 19, 123).

Sp.gr. at 15°	Per cent. of acid in solution	Sp.gr. at 15°	Per cent. of acid in solution
1·0045	1	1·1505	30
1·0090	2	1·1560	31
1·0136	3	1·1615	32
1·0179	4	1·1670	33
1·0224	5	1·1726	34
1·0273	6	1·1781	35
1·0322	7	1·1840	36
1·0371	8	1·1900	37
1·0420	9	1·1959	38
1·0469	10	1·2019	39
1·0517	11	1·2078	40
1·0565	12	1·2138	41
1·0613	13	1·2198	42
1·0661	14	1·2259	43
1·0709	15	1·2317	44
1·0761	16	1·2377	45
1·0813	17	1·2441	46
1·0865	18	1·2504	47
1·0917	19	1·2568	48
1·0969	20	1·2632	49
1·1020	21	1·2696	50
1·1070	22	1·2762	51
1·1124	23	1·2828	52
1·1175	24	1·2894	53
1·1227	25	1·2961	54
1·1282	26	1·3027	55
1·1338	27	1·3093	56
1·1393	28	1·3159	57
1·1449	29	1·3220	57·9

Strong solutions of tartaric acid contract on dilution. Thus 500 c.c. of a solution of sp.gr. 1·338 require 505·508 volumes of water to produce 1000 volumes (Warrington, Journ. Chem. Soc. 1875, 942). The presence of much free sulphuric acid diminishes the solubility of tartaric acid at ordinary temperatures and increases the difference between the solubility at low and high temperatures. A cold saturated solution of tartaric acid, when mixed with half its volume of strong sulphuric acid and cooled, gives an abundant white precipitate of tartaric acid, whilst a hot solution of the acid in one volume of water and one and half volumes of sulphuric acid (sp.gr. 1·713) deposits 70 p.c. of the tartaric acid on cooling. Thus a much larger proportion of tartaric acid is obtained in one crystallisation when sulphuric acid is present (Grosjean, Chem. Soc. Trans. 1883, 334).

The optical rotation $[\alpha]_D$ of aqueous solutions of the acid is given in the following table (Thomsen, J. pr. Chem. 1885, [ii.] 32, 318; cf. Kanonnikoff, J. Russ. Phys. Chem. Soc. 1890, 22, 369; Přibram and Glücksmann, *l.c.*).

Pert cent. of acid	10°	15°	20°	25°	30°
50	5·93	6·67	7·38	8·03	8·64
40	7·58	8·26	8·91	9·51	10·07
30	9·22	9·85	10·45	10·99	11·50
20	10·87	11·44	11·98	12·47	12·93

In supersaturated aqueous solutions the rotation falls to 0°, and finally becomes lævo-rotatory (Lepeschkin, Ber. 1899, 32, 1180). In benzene-alcohol solution, *d*-tartaric acid gives a lævo-rotation for all the rays from $\lambda=0\cdot578$ to $0\cdot436\mu$, the dispersion being normal, $[\alpha]_{436}/[\alpha]_{578}=4\cdot45$ at 21°. In the presence of neutral salts of strong acids, in particular in the presence of calcium chloride, the dextro-rotation of tartaric acid in aqueous solution diminishes and becomes an increasing lævo-rotation as the concentration of the calcium chloride increases. The dispersion, which is at first abnormal, becomes normal by the addition of a suitable amount of calcium chloride (R. de Malleman, Compt. rend. 1920, 171, 950; Chem. Soc. Abstr. 1921, i. 7; see also *ibid.* i. 158). In a mixture of dry ether and acetone the rotation is also lævo-rotatory (Landolt, *ibid.* 1880, 13, 2329). For rotation in solutions of ether and alcohol, v. Přibram, Monatsh. 1888, 9, 488. For rotation in aqueous solutions of inorganic salts, see Clough (Chem. Soc. Trans. 1914, 105, 49). For the changes in the rotatory power of fused and undercooled tartaric acid at various temperatures, see Bruhat (Trans. Faraday Soc. 1914, 10, 84; Ann. Chim. 1915, [ix.] 3, 121). For the inversion of rotation of derivatives of tartaric acid, see De Malleman (Chem. Soc. Abstr. 1921, ii. 614). For the rotatory power of metallic and amine esters of tartaric acid, see Casale (Chem. Soc. Abstr. 1917, 378). For the optical rotation of tartaric acid and its derivatives, see Clough (Chem. Soc. Proceedings, 1913, 352; Chem. Soc. Trans. 1914, 51; Proceedings 307; Chem. Soc. Trans. 1915, 96; see also Bruhat, Chem. Soc. Abstr. 1915, i. 496).

The anomalous rotatory dispersion of tartaric acid was attributed by Arndtsen in 1858 to the superposition of the opposite normal rotation of two forms of the acid, which have recently been described by Longchambon as α - and β -tartaric acid. Longchambon's view that the lævo-rotatory α form of the acid is identical with that which exists in the crystals (which give a normal lævo-rotation) is accepted; it is, however, urged that dilution with a large excess of water does not give the pure β -acid, but a dextro-rotatory equilibrium mixture of the α - and β -acids. This opinion is based on the fact that the anomalies are not removed by dilution, although they disappear completely in presence of boric acid or when the acid is converted into tartar emetic $\text{KSbO}(\text{C}_4\text{H}_4\text{O}_6)$ (Lowry and Austin, *Compt. rend.* June, 1924, 178, 1902; *Sci. Abstr.* 1924, 27, 796). For the rotatory dispersion of tartaric acid and its salts, see Lowry and Austin (*Chem. Soc. Abstr.* 1922, ii. 414); Bruhat (*ibid.* 1920, ii. 404); see also POLARIMETRY, vol. v. 349. For the Rotatory Dispersive Power of Organic Compounds, Part xi., The Molecular Weight of Ethyl Tartrate and the Origin of Anomalous Rotatory Dispersion in Tartaric Acid and its Derivatives, see Lowry and Cutler (*J. Chem. Soc.* 1924, 125, 1465). According to Patterson and Moudgill (*Chem. Soc. Abstr.* 1919, ii. 377), rotation-temperature curves have been produced from measurements of the rotation of ethyl *d*-tartrate and isobutyl dibenzoyl-*d*-tartrate dissolved in cinnamaldehyde and ethylene dibromide respectively at a series of temperatures from 0.181° in the first-named solvent and 17.7° and 39.7° in the last-named solvent. A consideration of the present and previously published results (*Chem. Soc. Trans.* 1908, 93, 1844; 1912, 101, 378; 1913, 103, 152; 1916, 109, 1145) shows that a general temperature-rotation curve may be produced for all tartrates. The change in the solution of the superfused acid takes place in two stages: (1) a rapid modification, finished in a few hours, marked by a diminution in the rotation, probably due to the conversion of metatartaric acid into tartaric acid; and (2) a slow modification lasting several months, which produces a diminution of the rotation for pure tartaric acid, due to the transformation of ditartaric acid into tartaric acid and accompanied by a gradual increase of acidity of the solution. According to Aignan tartaric acid exists in solution as the polymeride $(\text{C}_4\text{H}_6\text{O}_6)_2$ which is partially dissociated (*Compt. rend.* 1891, 112, 951). Affinity constant, $k=0.097$ (Walden, *Ber.* 1896, 29, 1701); dissociation constants, $k_1=970.0 \times 10^{-6}$; $k_2=59.0 \times 10^{-6}$ (Smith, *Zeitsch. physikal. Chem.* 1898, 25, 193). Molecular refraction *v.* Gladstone and Hibbert, *Chem. Soc. Trans.* 1897, 824. Conductivity *v.* Bischoff and Walden, *l.c.*; Ostwald, *Zeitsch. physikal. Chem.* 1889, 3, 371.

On heating tartaric acid at its melting-point some *ditartaric acid* is stated to be produced together with a variety of tartaric acid known as *metatartaric acid*. This acid is an amorphous deliquescent mass, the solution of which regenerates *d*-tartaric acid on boiling. It yields salts of greater solubility than the *d*-tartrates into which they are converted on boiling with water (Grosjean, *Chem. Soc. Trans.* 1883, 334; Erdmann, *Annalen*, 1837, 21, 9; Laurent and

Gerhardt, *ibid.* 1849, 70, 348; Braconnot, *Ann. Chim.* [ii.] 68, 299). By heating at 180° , or for a considerable time at 150° , *ditartaric acid* (*tartralic acid*) is obtained, while the further action of heat yields *tartrelic acid* (*soluble tartaric anhydride*) and *tartaric anhydride*. Ditartronic acid $\text{C}_8\text{H}_{10}\text{O}_{11}$ is an amorphous very deliquescent substance which readily combines with water, especially on boiling, to regenerate tartaric acid. Tartrelic acid $\text{C}_4\text{H}_4\text{O}_5$ forms yellow deliquescent crystals which are converted by boiling water first into ditartaric acid and then into tartaric acid. Tartaric anhydride $\text{C}_4\text{H}_4\text{O}_5$ is a colourless powder, insoluble in water, alcohol, or ether, but is converted by boiling water first into tartrelic acid, then into ditartaric acid and finally into tartaric acid (Warrington, *l.c.*; Frémy, *Annalen*, 1839, 29, 444; Laurent and Gerhardt, *Compt. rend.* 1848, 27, 318; Schiff, *Annalen*, 1863, 125, 129).

The dry distillation of tartaric acid yields pyruvic acid, pyrotartaric acid, pyrotritaric acid, $\text{C}_7\text{H}_8\text{O}_7$, uvitic acid $\text{C}_7\text{H}_8\text{O}_2$, and acetic acid. These decompose yielding carbon monoxide, carbon dioxide, acetaldehyde, acetone, formic acid, and other compounds (Vöckel, *Annalen*, 1854, 89, 57; Bourgoin, *Bull. Soc. chim.* 1878, [ii.] 29, 309; Pelouze, *Ann. Chim.* [ii.] 46, 297; Böttger, *Ber.* 1876, 9, 670; Liebermann, *ibid.* 1882, 15, 428). When tartaric acid is decomposed at the lowest possible temperature and under diminished pressure it first yields water and then a mixture of carbon monoxide and carbon dioxide, together with formic, acetic, and pyruvic acids. The other substances above mentioned are probably due to secondary reactions (Chattaway and Ray, *Chem. Soc. Trans.* 119, 1921, 34). Fusion with potassium hydroxide yields acetic and oxalic acids. By destructive distillation with potassium hydrogen sulphate an acid isomeric with pyrotritaric acid is obtained (Simon, *Compt. rend.* 1900, 131, 586). By heating tartaric acid with water, hydrochloric acid or alkali, racemic and *mesotartaric* acids are obtained in varying proportions (*v. Racemic acid, infra*). By oxidation with chromic acid, potassium permanganate or sulphuric acid, carbon dioxide and formic acid are obtained, whilst if slowly oxidised with nitric acid, tartaric acid is the product. Phosphorus and hydriodic acid reduce tartaric acid to malic and succinic acids. Phosphorus pentachloride yields chlorofumaric chloride.

By oxidising tartaric acid in the presence of a ferrous salt *dihydroxymaleic acid* $\text{C}_4\text{H}_4\text{O}_6 \cdot 2\text{H}_2\text{O}$ is obtained. On reduction of the latter the final product is succinic acid, whilst on oxidation with glacial acetic acid and bromine *dihydroxytartaric acid* is produced, which is a good reagent for the detection of sodium salts (Fenton, *Chem. Soc. Trans.* 1895, 48; 1896, 546; 1898, 71, 472; Eng. Pat. 26259).

For the oxidation of tartaric acid by potassium permanganate and hydrogen peroxide, see W. Meigen and I. Schnerb (*Zeitsch. angew. Chem.* 1924, 37, 208; *Chem. Soc. Abstr.* 1924, ii. 506).

On exposure of a solution of tartaric acid to light for a year in a stoppered flask, Otto found that part was converted into pyruvic acid, although no micro-organisms were present

(Ber. 1895, 27, 838, 1264). It is stated by Wehmer that a mould develops in pure tartaric acid solutions and is capable of existence in the presence of large amounts of acid. This mould produces citric acid fermentation in sugar solutions (Bied. Zentr. 1898, 27). On exposure of a 5 p.c. aqueous solution containing 1 p.c. uranium oxide to the action of sunlight, the first products are oxalic acid and a compound $C_2H_4O_2$ which reduces cupric salts. The oxalic acid is then converted into water, carbon dioxide and carbon monoxide and the last-named reduces part of the tartaric acid to malic acid and then to succinic acid. At the same time part of the malic acid is converted into oxalic acid and acetaldehyde and the succinic acid into propionic acid and carbon dioxide (Seekamp, Annalen, 1894, 278, 810).

For the decomposition of tartaric acid in ultra-violet light, see Euler and Ryd (Chem. Soc. Abstr. 1913, ii. 544).

Yeast ferments tartaric acid solutions yielding butyric and propionic acids, the latter being probably formed through the intermediate production of glyceric, malic, and succinic acids. Acetaldehyde is also present in small quantity (Karczag, Biochem. Zeitsch. 1912, 43, 44). On the purification of brewing yeast from wild yeasts by tartaric acid, v. Hansen, Zeitsch. Brauwesen, 1892, 2; Lindner, Wochenschrift Braueri, 12, 316).

By the interaction of tartaric acid and trioxymethylene or formaldehyde under suitable conditions monomethylene- and dimethylene-tartaric acids can be obtained (Henneberg and Tollens, Annalen, 1896, 292, 53; van Ekenstein, Proc. K. Akad. Wetensch. Amsterdam, 1900, 3, 400; Rec. trav. chim. 1901, 20, 331; Sternberg, Pharm. Zeit. 1901, 46; Chem. Fabr. auf Aktien von E. Schering, D. R. P. 130346, Chem. Soc. Abstr. 1902, i. 705; de Bruyn and van Ekenstein, Rec. trav. chim. 1902, 21, 310). By the action of formaldehyde on tartaric acid two compounds can be obtained, one of which is strongly dextro- the other lævo-rotatory. These have been examined in order to obtain further evidence on the nature of the dynamic isomerides which are present in aqueous solutions of *d*-tartaric acid of all concentrations (Lowry and Austin, Phil. Trans. Roy. Soc. A. 1922, 222, 249). Methylene-tartaric acid, prepared by a modification of the method of Lobry de Bruyn and van Ekenstein (Rec. trav. chim. 1902, 21, 313), was found to possess a specific rotation $[\alpha]_D^{20} = -81.3^\circ$ for solutions of different concentrations. Its rotatory dispersion is simple, *i.e.* it is expressed by one term of Drude's equation. Dimethylene tartrate, on the other hand, is strongly dextro-rotatory, but its rotatory dispersion is also simple. Alternative formulæ are suggested for the latter compound. It is claimed that the complex character of the dispersion of tartaric acid is due to an oscillation of the molecule between two configurations, since this oscillation is prevented by bridging across the hydroxylic groups, when derivatives of simple dispersion result (P. C. Austin and V. A. Carpenter, J. Soc. Chem. Ind. 1924, 43, B. 331). Tartaric acid gives a dinitrate in 81 p.c. yield on treatment with nitrogen pentoxide (Gibson, Proc. Roy. Soc. Edinburgh, 1908, 28, 705). When iron is placed

in a solution of tartaric acid, hydrogen is evolved and the compound $C_4H_2O_6Fe_2$ is produced, showing that both the carboxylic and alcoholic hydrogen atoms have been replaced (Ulsch, Chem. Zeit. 1899, 23, 658).

For the action of uranyl acetate on tartaric acid and its salts, see Kopatschek (Chem. Soc. Abstr. 1922, i. 984). For the reactions of potassium sulphate with tartaric acid, see Bornträger (Chem. Soc. Abstr. 1919, i. 522).

For the variation in properties of isomeric forms of tartaric acid, see Berner (Chem. Soc. Abstr. 1920, ii. 13).

Uses. Tartaric acid is used in certain photographic processes for printing and developing. It is also employed medicinally and for the production of baking powders, effervescent drinks, Seidlitz powders, &c. It is used by the calico printer to liberate chlorine from bleaching powder, and in the production of a number of dyestuffs; as a 'resist' for aluminium and other mordants and in the discharge colours for Turkey-red. It is also used in the mordant bath in dyeing wool; for brightening the colour of silk after dyeing; and for tendering cotton fibre.

Salts. Tartaric acid contains four hydrogen atoms which can be replaced by metals, but only two of these are in carboxyl groups, and hence the acid is dibasic forming two series of salts, the tartrates and the hydrogen tartrates or 'bitartrates'. Few of the salts are readily soluble in water and all are insoluble in alcohol.

For the metallic salts of tartaric acid, see Pickering (Chem. Soc. Trans. 1916, 236; *ibid.* Abstr. i. 306). For the complex cupric salts of tartaric acid, see Packer and Wark (Chem. Soc. Trans. 1921, i. 1348).

Potassium hydrogen tartrate, cream of tartar, $C_4H_5O_6K$, occurs in the juice of the grape and is deposited on fermentation on account of its lesser solubility in alcohol, partly as a crystalline crust known as 'argol' and partly with the 'lees.' The argol, &c., when heated with water, yields slightly coloured crystals of the purer salt which is known as 'tartar.' This may be further purified by any of the methods given under the manufacture of tartaric acid.

Potassium hydrogen tartrate crystallises in aggregates of small hard rhombic prisms, having a sp.gr. of 1.973 (Schiff, Annalen, 1859, 112, 89; cf. Schabus, J. 1850, 377; Buignet, *ibid.* 1861, 15; Cooke, *ibid.* 1880, 805). Its solubility in water and aqueous alcohol is given in the table on p. 688 (Roelofsen, Amer. Chem. J. 1894, 16, 466; cf. Wenger, *ibid.* 1892, 14, 624; Blarez, Compt. rend. 1891, 112, 434, 808; Noyes and Clement, Zeitsch. physikal. Chem. 1894, 13, 413; Maganani, Gazz. chim. ital. 1901, 31, ii. 542).

The solubility is diminished by the presence of tartaric acid and increased by the presence of other acids. These results are of great importance in the estimation of tartaric acid as potassium hydrogen tartrate. Mineral acids should not be present, nor any large excess of potassium acetate or citrate. The solubility of potassium hydrogen tartrate in water is greatly diminished if potassium sulphate, nitrate, or, especially, chloride be present. Grosjean showed that while the solubility in water at 12° was 1 in 262, the solubility in a 5 p.c. solution of potassium chloride was 1 in 3213, and in a 10 p.c. solution 1 in 4401. For con-

ductivity of aqueous solutions, *v.* Walden, Zeitsch. physikal. Chem. 1891, 8, 466.

The alteration of the solubility in water caused by the presence of other substances has been determined by Warington (Journ. Chem. Soc. 1875, 947; *cf.* Magnanini, *l.c.*; Noyes and Clement, *l.c.*; Blarez, *l.c.*). The following table gives the solubility at 14° in acid solutions of equal acidity, *i.e.* of such strength that equal volumes require the same amount of alkali for neutralisation; and in potassium acetate and citrate:—

—	Grms. of acid or salt in 100 c.c.	Grms. of KHTa dissolved in 100 c.c.
Water	—	0·422
Acetic acid	0·8106	0·422
Tartaric acid	1·0331	0·322
Citric acid	0·8448	0·546
Sulphuric acid	0·6853	1·701
Hydrochloric acid	0·5037	1·949
Nitric acid	0·8445	1·969
Potassium acetate	1·3875	0·744
Potassium citrate	1·3966	0·843

Potassium hydrogen tartrate has been proposed as a standard for acidimetry and alkali-metry (Bornträger, Zeitsch. anal. Chem. 1892, 31, 43; 1894, 33, 713; Zeitsch. angew. Chem. 1894, 54; Kollo, Pharm. Zentr.-h. 1909, 50,

315; Hefelman, *ibid.* 334). To prepare pure potassium hydrogen tartrate for this purpose, white cream of tartar is heated with dilute hydrochloric acid, the solution cooled and stirred, and the precipitate filtered, washed, and recrystallised from hot water. Or a solution of tartaric acid may be divided into two equal parts, one portion being neutralised with potassium carbonate and the other portion added to it. The precipitate is washed and recrystallised from hot water. It is quite pure when the alkali obtained by calcining a weighed quantity exactly neutralises an equal weight of the uncalcined substance, neutral litmus paper being used as an indicator.

When heated, potassium hydrogen tartrate yields a mixture of carbon and potassium carbonate used as a reducing agent under the name of ‘black flux.’ Potassium hydrogen tartrate is used in the preparation of effervescing drinks, baking powders, &c., and in medicine; also in the mordant bath for wool dyeing, in conjunction with alum, iron salts, stannous chloride, &c., apparently producing double salts which are more effective as mordants.

Cream of tartar dissolves readily in a solution of boric acid or borax (Le Fèvre, Mémoires de L’Acad. Royale, Paris, 1732), and the product is used medicinally under the name ‘soluble cream of tartar.’ It is best prepared by dissolving a mixture of 4 parts of cream of tartar and 1 of boric acid in 24 parts of water and heating

Temperature	Milligrams of C ₄ H ₅ O ₆ K in 10 c.c.									
	Percentage of alcohol									Water
	90	80	70	60	50	40	30	20	10	
0°	6·2	6·4	4·9	6·0	6·0	6·2	7·0	10·8	17·3	30·1
5°	5·5	6·0	5·1	6·0	6·8	6·8	7·1	13·2	18·8	32·0
10°	6·2	6·2	5·1	5·8	6·4	7·0	8·6	16·0	27·0	41·1
15°	5·3	6·2	6·2	6·2	5·5	7·7	8·8	15·8	23·9	44·3
20°	6·4	6·4	6·2	6·4	7·0	9·6	11·3	17·1	29·3	49·0
25°	4·7	5·5	6·0	6·8	7·0	10·3	11·7	21·4	36·4	54·1
30°	4·7	6·0	6·8	7·5	8·5	11·0	13·1	24·8	39·9	69·2
35°	1·9	5·1	5·9	6·8	9·0	12·4	18·8	28·7	49·3	83·8
40°	1·7	5·3	5·8	7·0	10·2	14·9	23·1	37·7	53·6	95·9
45°	1·7	5·3	6·0	7·9	10·7	16·5	25·8	44·2	72·6	112·8
50°	1·5	5·1	6·0	8·1	12·8	19·0	29·7	53·6	87·2	124·8

until most of the water is driven off. The salt prepared with boric acid is a white powder, which is permanent in the air, whereas that prepared with borax, and known in the German Pharmacopœia as ‘Boraxweinstein’ is deliquescent.

Potassium hydrogen tartrate dissolves many oxides, forming double tartrates; tartar emetic is a compound of this nature (*v.* ANTIMONY). Other double salts which have been prepared in a similar manner are the *titanitartrates* and *stannitartrates* (Henderson, Orr and Whitehead, Chem. Soc. Trans. 1899, 556; *cf.* Rosenheim and Schütte, Zeitsch. anorg. Chem. 1901, 26, 239); *molybdotartrates* (Henderson and Barr, Chem. Soc. Trans. 1896, 1445; *cf.* Rosenheim and Itzig, Ber. 1900, 33, 707; Itzig, *ibid.* 1901, 34, 1372);

glucinetartrates (Rosenheim and Woge, Zeitsch. anorg. Chem. 1897, 15, 299); *tartrarsenites* (Henderson and Ewing, Chem. Soc. Trans. 1895, 103). The *tungstotartrates* are prepared by boiling tungstic acid in a solution of a normal alkali tartrate (Rosenheim and Itzig, *l.c.*).

Potassium ferric tartrate is prepared by adding precipitated ferric hydroxide to potassium hydrogen tartrate and treating with cold water. It is the *ferrum tartaratum* of pharmacy, and should yield 30 p.c. of Fe₂O₃ on ignition, as estimated from the weight of ash insoluble in water. It forms ruby-red transparent scales soluble in about 4 parts of water.

Potassium tartrate C₄H₄K₂·½H₂O is prepared by neutralising potassium hydrogen tartrate with potassium carbonate or hydroxide.

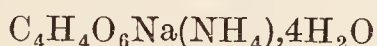
It forms colourless, monoclinic crystals, which have sp.gr. 1.973 (Schiff, *Annalen*, 1859, 112, 89) and are soluble in 66 parts of water at 14°, the solubility decreasing with rise of temperature. When a solution of this salt is treated with acid, potassium hydrogen tartrate is precipitated. By the electrolysis of a concentrated aqueous solution of potassium tartrate potassium hydrogen tartrate, carbon dioxide, carbon monoxide, a little formaldehyde and formic acid, but no acetic acid are produced (Miller and Hofer, *Ber.* 1894, 27, 468).

Sodium hydrogen tartrate $C_4H_5O_6Na, H_2O$ and *sodium tartrate* $C_4H_4O_6Na_2, 2H_2O$ crystallise in rhombic crystals (Dumas and Piria, *Annalen*, 1844, 44, 88). They are both very soluble; the normal salt dissolves in 2.28 parts of water at 24°, and the sp.gr. of the crystals is 1.794. For the toxicity of sodium tartrate, see Salant and Smith (*Chem. Soc. Abstr.* 1914, i. 1189).

Potassium sodium tartrate, Rochelle salt $C_4H_4O_6NaK, 4H_2O$ is prepared by neutralising potassium hydrogen tartrate with sodium carbonate or hydroxide. It forms large rhombic prisms of sp.gr. 1.767 (Schiff, *l.c.*), and is soluble in 1.70 parts of water at 6° (Fresenius, *Annalen*, 1845, 53, 234). Above 40° a saturated solution deposits crystals of Rochelle salt and sodium tartrate, and above 55° a mixture of potassium and sodium tartrates (van Leeuwen, *Zeitsch. physikal. Chem.* 1897, 23, 33). Addition of acetic acid to the solution precipitates potassium hydrogen tartrate, this reaction distinguishing Rochelle salt from sodium tartrate. Seidlitz powders contain Rochelle salt, which is sometimes replaced wholly or partly by sodium hydrogen carbonate. Some powders also contain about 0.001 grain of tartar emetic.

For the piezo-electricity of potassium sodium tartrate crystals, see Scott (*Chem. Soc. Abstr.* 1922, ii. 609). For the growth of crystals of potassium sodium salt, see Ishimoto (*ibid.* 1920, i. 708). For the use of potassium sodium salt in estimation of oxygen in water, see Van Eck (*ibid.* 1913, ii. 616).

Ammonium hydrogen tartrate $C_4H_5O_6NH_4$ and *ammonium tartrate* $C_4H_4O_6(NH_4)_2$ have similar properties to those of the corresponding potassium salts (Pasteur, *J.* 1853, 415; 1854, 395; Schiff, *l.c.*). For the ammonium tartrate, see McMaster (*Chem. Soc. Abstr.* 1913, i. 444). *Ammonium potassium tartrate* $C_4H_4O_6K(NH_4)$ and *ammonium sodium tartrate*



resemble Rochelle salt in their properties.

Ammonium ferric tartrate, which is employed in medicine, is prepared according to the U.S. Dispensatory, 14th ed. p. 1214, by dissolving 6 ozs. of tartaric acid in 2 pints of water and neutralising it with ammonium carbonate, 6 ozs. of tartaric acid being then added. Ferric hydroxide, precipitated from a solution of ferric chloride, is then stirred in at 140°F. until no more will dissolve. The solution is then filtered, evaporated to a syrup at a temperature below 140°F. and dried on a glass plate. It forms transparent garnet-red scales of sweetish taste, which are slowly but extremely soluble in water to a neutral solution, but insoluble in alcohol or ether.

The normal and acid tartrates of *lithium*, *cæsium*, and *rubidium* are all readily soluble. The rubidium salt crystallises from aqueous solutions in anhydrous, hexagonal, trapezohedral crystals, having sp.gr. 2.694 at 14°; they are lævo-rotatory (Traube, *Sitzungsber. Berl. Akad.* 1895, 10, 195).

Magnesium tartrate $C_4H_4O_6Mg, 4H_2O$ is obtained as a crystalline crust by evaporating a solution of magnesium carbonate in tartaric acid, and is soluble in 123 parts of water at 15.6°. The acid salt $(C_4H_5O_6)_2Mg$ is obtained by dissolving magnesium carbonate in excess of tartaric acid. It is a crystalline substance, soluble in 53 parts of water at 15.6°. Double salts with the alkali metals are known (Mayer, *Annalen*, 1857, 101, 166; Dulk, *ibid.* 1832, 2, 59; Makovetzki, *J. Russ. Phys. Chem. Soc.* 1906, 38, 769).

Calcium tartrate $C_4H_4O_6Ca, 4H_2O$ occurs in small quantities, together with the acid potassium salt, in many plants and is always found in argol and lees as described previously. It may be prepared by adding excess of calcium chloride to a solution of a tartrate. It crystallises in rhombic prisms or pyramids, but is frequently deposited from dilute solutions in aggregates of fine radiating needles containing 6 mols. H_2O which are transformed rapidly into the orthorhombic tetrahydrate. For the crystallisation of calcium tartrate, see Chattaway (*J. Amer. Chem. Soc.* 1916, 38, 2519). The solubilities of the tartrates of calcium, strontium, and barium are given in the following table (Cantoni and Zachoder, *Bull. Soc. chim.* 1904, [iii.] 31, 1121; Herz and Muhs, *Ber.* 1903, 36, 3716; Anschütz, *Annalen*, 1884, 226, 197; Dulk, *J. Chem. Phys.* 1832, 64, 180, 193; Neumann, *ibid.* 206; cf. Enell, *Zeitsch. anal. Chem.* 1899, 38, 368):—

Temp.	Grms. of salt in 100 c.c. water		
	$C_4H_4O_6Ca, 4H_2O$	$C_4H_4O_6Sr, 3H_2O$	$C_4H_4O_6Ba$
0°	0.0365	0.112	0.0205
10°	0.0401	0.149	0.0242
20°	0.0475	0.200	0.0279
25°	0.0525	0.224	0.0297
30°	0.0631	0.252	0.0315
40°	0.0875	0.328	0.0352
50°	0.1100	0.407	0.0389
60°	0.1262	0.480	0.0440
70°	0.1430	0.580	0.0480
80°	0.1798	0.680	0.0527
85°	0.2190	0.755	0.0541

Strong acids and potassium hydrogen tartrate dissolve calcium tartrate, and hence it is frequently present in purified tartars. It is precipitated from these solutions by ammonium hydroxide immediately or after some time. It is soluble in ammonium chloride and cold alkali, being reprecipitated from the latter on boiling. Alkali chlorides dissolve it more readily than does water (Cantoni and Jolkowsky, *Bull. Soc. chim.* 1907, [iv.] 1, 1181). A hot neutral solution of copper chloride converts it on digestion into insoluble copper tartrate, this reaction

distinguishing it from calcium citrate; this test, however, will not detect calcium tartrate in the presence of much calcium citrate. Unlike calcium racemate and calcium oxalate, calcium tartrate is soluble in acetic acid.

Calcium *d*-tartrate is precipitated in crystalline form from the solution of tartaric acid to be analysed by addition of a solution of calcium acetate and alcohol, the salt being finally dried in the air and weighed. The results are accurate to about 1 p.c. At 20° 1 litre of water dissolves 0.232 gm. of calcium *d*-tartrate, 0.249 gm. of calcium *l*-tartrate, and 0.493 gm. of calcium racemate respectively; 1 litre of 32 p.c. alcohol dissolves only 0.038 gm. of calcium *d*-tartrate (M. François and C. Lormand, *J. Pharm. Chim.* 1923, 28, 433; *J. Soc. Chem. Ind.* 1924, 43, B. 152).

Crude calcium tartrate is liable to undergo decomposition either by an anaerobic ferment, which yields formic, acetic, butyric, and higher fatty acids, but not propionic acid; or by an aerobic ferment yielding calcium carbonate as the ultimate product (Ordonneau, *ibid.* 1911, [iv.] 9, 398; cf. Emmerling, *Centr. Bakt. Par.* 1908, [ii.] 21, 317). *Bacillus Tartaricus*, which is capable of anaerobic and aerobic life, but which is more active in the latter state, decomposes calcium tartrate with the formation of acetic and succinic acids, hydrogen and carbon dioxide (Grimbert and Ficquet, *J. Pharm. Chim.* 1898, [vi.] 7, 97).

Calcium hydrogen tartrate $(C_4H_5O_6)_2Ca$ is formed by dissolving the normal salt in tartaric acid, and is much more soluble than the normal salt, 100 parts of water dissolving 0.71 part of the acid salt at 15.6°.

Strontium tartrate $C_4H_4O_6Sr \cdot 3H_2O$ and barium tartrate $C_4H_4O_6Ba$. Solubility (p. 689) (Cantoni and Zachoder, *Bull. Soc. chim.* 1904, [iii.] 31, 1122; Marignac, *Ann. Min.* 1859, [v.] 35, 280; Dulk and Neumann, *J. Phys. Chem.* 1832, 64, 180, 193; Scacchi, *Ann. Chem.* 1860, [ii.] 109, 373). A tribasic barium tartrate has been prepared by Quartaroli (*Staz. sperim. agrar. ital.* 1910, 43).

Aluminium tartrate $(C_4H_4O_6)_3Al_2$ is formed by dissolving alumina in tartaric acid and is a gummy non-deliquescent mass soluble in water; the solution is capable of dissolving considerable quantities of alumina without becoming alkaline. A double salt of potassium and aluminium appears to be formed by dissolving alumina in cream of tartar. It forms an amorphous mass not precipitated by alkalis, and probably constitutes the active ingredient of the mixture of alum and cream of tartar used in the mordant bath for dyeing wool.

For the aluminium sodium salts, see Vereinigte Fabriken für Laboratoriumsbedarf (*Chem. Soc. Abstr.* 1913, i. 1052).

Ferrous tartrate $C_4H_4O_6Fe$ is obtained as a white, almost insoluble, crystalline powder by boiling iron filings with tartaric acid. 100 parts of water at 15.6° dissolve 0.877 part of the salt (Dulk, *Annalen*, 1832, 2, 62; Méhu, *Jahrb.* 1873, 569).

Ferric tartrate $(C_4H_4O_6)_3Fe_2$ is obtained by dissolving the precipitated hydroxide in tartaric acid. The solution deposits a basic salt on warming, but is not precipitated by addition of alkalis on account of the production of a double

salt (cf. Rosenthaler and Siebeck, *Arch. Pharm.* 1908, 246, 51; Pickering, *Chem. Soc. Trans.* 1913, 103, 1354, 1362. See also *Chem. Soc. Proceedings*, 1913, 191).

Manganous tartrate $MnC_4H_4O_6 \cdot 2H_2O$, prepared by adding an equimolecular solution of sodium or potassium tartrate to manganous sulphate or chloride solutions. Small rose-tinted monoclinic crystals. Loses 14 p.c. of its water at 100°, and continues to lose water up to 180°, and at 200° darkens with decomposition (Dobbin, *J. Amer. Chem. Soc.* 1919, 41, 934).

Nickel tartrate and cobalt tartrate and double salts with potassium tartrate are described by Tower (*J. Amer. Chem. Soc.* 1900, 22, 501; cf. Werther, *J. pr. Chem.* 1844, [i.] 32, 400; Fabian, *Annalen*, 1857, 103, 248; Pickering, *Chem. Soc. Trans.* 1915, 107, 942; *Abstr.* ii. 637).

Zinc tartrate $C_4H_4O_6Zn \cdot 2H_2O$ is prepared by the action of tartaric acid on zinc acetate (Schiff, *Annalen*, 125, 146) or by boiling tartaric acid with zinc (Frisch, *J.* 1866, 410). The solubility of zinc, copper, and lead tartrates is given in the following table (Cantoni and Zachoder, *Bull. Soc. chim.* 1905, [iii.] 33, 754; cf. Partheil and Hübner, *Arch. Pharm.* 1903, 241, 413):—

Temp.	Grms. of salt in 100 c.c. water		
	$C_4H_4O_6Zn \cdot 2H_2O$	$C_4H_4O_6Cu \cdot 3H_2O$	$C_4H_4O_6Pb$
15°	0.019	0.0197	0.0
20°	0.022	0.0420	—
25°	0.036	0.0690	—
30°	0.041	0.0890	—
40°	0.060	0.1420	0.0015
50°	0.087	0.1920	0.00225
55°	0.116	0.2124	0.00295
60°	0.104	0.1970	0.00305
70°	0.088	0.1640	0.0032
80°	0.059	0.1440	0.0038
85°	0.041	0.1370	0.0054

Copper tartrate $C_4H_4O_6Cu \cdot 3H_2O$ is obtained as a greenish-blue crystalline powder on addition of copper sulphate to a soluble tartrate. It dissolves in alkalis and ammonia with formation of double tartrates and the deep blue solution is reduced, with precipitation of cuprous oxide, by heating with glucose and many other organic compounds (v. BARRESWIL'S (FEHLING'S) SOLUTION). For solubility v. *supra*.

Lead tartrate $C_4H_4O_6Pb$ is prepared by the addition of tartaric acid to a soluble lead salt when it forms a white crystalline powder (sp.gr. 3.871) almost insoluble in water (v. *supra*), but readily dissolved by alkalis. It is also obtained by boiling lead acetate with tartaric acid (Heintz, *J.* 1860, 261; Frisch, *ibid.* 1866, 400). By boiling an ammoniacal solution of the normal tartrate, the insoluble basic tartrate $C_4H_2O_6Pb_2$ is obtained (Erdmann, *Annalen*, 1837, 21, 19).

Silver tartrate v. SILVER.

Antimony tartrate v. ANTIMONY; also Blanchetière, *Bull. Soc. chim.* 1920, [iv.] 27, 477.

Bismuth tartrate.—According to Baudran on boiling bismuth hydroxide with tartaric acid,

bismuthotartaric acid $C_4H_5O_6(BiO),H_2O$ is obtained, and by replacement of a hydrogen atom by potassium, an emetic is produced. Similar salts may be obtained containing manganese, iron, or chromium in place of bismuth (Ann. Chim. 1900, [vii.] 14, 506). Telle states that the compound forms small needles and has the constitution $C_8H_9O_{12}Bi,3H_2O$, and that it may also be obtained by adding tartaric acid to the hydrated lactate of bismuth (Arch. Pharm. 1908, 246, 484). It is almost insoluble in water. Fischer and Grützner state that by boiling freshly precipitated bismuth hydroxide with tartaric acid the compound $C_4H_4O_6,2Bi(OH)_2$ is formed as a white, amorphous, electrical precipitate (*ibid.* 1894, 232, 460).

Bismuth tartrates prepared by precipitation are not well-defined compounds, but mixtures of oxytartrates; when the latter are digested in tartaric acid solution a crystalline compound is obtained having a composition corresponding with the formula $Bi_2(C_4H_4O_6)_2,2H_2C_4H_4O_6$. There appears to be no uniformity in the composition of the different commercial preparations of the alkali bismuth compounds, and the authors have not been able to obtain a compound analogous to tartar emetic (C. E. Corfield and F. W. Adams, Pharm. J. 1923, iii. 82-85; J. Soc. Chem. Ind. 1923, 92, 950 A; *cf.* Corfield and Adams, Pharm. J. 1924, 113, 86).

In the absence of oxygen, tartaric acid has very little action on tin (Hall, J. Amer. Chem. Soc. 1883, 4, 440; Lehmann, Arch. Hygiene, 1907, 63, 67). In presence of oxygen *Stannous tartrate* is formed, colloidal stannous or stannic hydroxide going into solution (Chapman, Chem. Soc. Trans. 1913, 103, 775).

According to V. Volmar (Compt. rend. 1923, 176, 742, 1465-1467; solutions of potassium antimonyl tartrate and the corresponding compounds of arsenic, bismuth, copper, and iron undergo decomposition on exposure to ultraviolet light with liberation of the metal, the maximum effect being produced in the case of the bismuth compound. The simple salts of the same metals, both organic and inorganic, are quite stable under similar conditions. The conclusion is drawn that the heavy metal in the tartrates occupies a position in the molecule in accordance with the constitution attributed to it by Jungfleisch. Potassium borotartrate furnishes an exception; the author considers this to be due to the fact that it appears to be not a definite compound but a mixture (J. Chem. Soc. 1923, 124, ii. 279, 453).

Tartaric esters. The normal esters of tartaric acid may be prepared (i.) by saturating a solution of tartaric acid in the alcohol required with hydrogen chloride; (ii.) by heating an alkyl hydrogen tartrate in a sealed tube with the corresponding alcohol; (iii.) by the action of an alkyl iodide on silver tartrate. If the last method be used a small quantity of the alkyl dialkyloxy compound is also formed, and this has a high rotation (Rodger and Brame, Chem. Soc. Trans. 1898, 301; Purdie and Lander, *ibid.* 1899, 156).

Methyl tartrate $C_4H_4O_6(CH_3)_2$ is a crystalline solid, m.p. 48° ; b.p. 280° , $163^\circ/23$ mm.; sp.gr. 1.3403 at 15° (in liquid state); $\alpha_D + 2.74^\circ$. It remains liquid below its melting-point for a

considerable time (Anschütz and Pictet, Ber. 1880, 13, 1176; Anschütz, *ibid.* 1885, 18, 1399; Frankland and Wharton, Chem. Soc. Trans. 1896, 1310).

Dimethyl ester. For the association of the dimethyl ester in benzene, see Innes (Chem. Soc. Trans. 1918, 433).

Ethyl tartrate $C_4H_4O_6(C_2H_5)_2$ purified by distillation, freezing and redistillation *in vacuo* freezes at 18.7° and gives $[\alpha_{5461}] + 55.9^\circ$ in a 6 dm. tube at 20° , $[\alpha_{5461}] + 7.87$. The density of the ester at 20° is 1.2028, and its viscosity 2.217 C.G.S. units. When sufficiently purified, the ester becomes yellow on heating, and appears to decompose at atmospheric temperatures *in vacuo* in presence of phosphoric oxide. For the production of the green colour in the preparation of ethyl tartrate, see Patterson (Chem. Soc. Trans. 1922, 1042). The influence of solvents, temperature, &c., on the rotation of ethyl tartrate has received considerable attention, *v.* POLARIMETRY and following references: Frankland, *ibid.* 1899, 349; Patterson, *ibid.* 1901, 167, 477; 1903, 765; 1905, 313; 1908, 1836; Patterson and McMillan, *ibid.* 1907, 504; Patterson and McDonald, *ibid.* 1908, 936; 1909, 321; 1916, 1139; Patterson and Montgomerie, *ibid.* 1130; Patterson and Anderson, *ibid.* 1912, 1833; Purdie and Barbour, *ibid.* 1901, 871; Grossmann, Zeitsch. physikal. Chem. 1910, 73, 148; Peacock, Chem. Soc. Trans. 1915, 107, 1547; *ibid.* Abstr. 1916, ii. 4; Lowry and Dickson, *ibid.* 1915, 107, 1173; *ibid.* Abstr. ii. 660; Patterson, Chem. Soc. Trans. 1916, 1139; *ibid.* Abstr. 1917, ii. 3, 4, 5). For the preparation and properties of pure ethyl tartrate, see Lowry and Cutter (Chem. Soc. Trans. 1922, 121, 532). By passing hydrogen chloride into ethyl alcohol and then adding methyl tartrate and finally boiling under a reflux apparatus, ethyl tartrate is produced. The reverse reaction may also be accomplished (Patterson and Dickinson, Chem. Soc. Trans. 1901, 280). Alkyl metallic salts of the type $C_4H_4O_6RM$ have been prepared.

The *l*-menthylurethane of ethyl *d*-tartrate has $[\alpha]_C - 58.31^\circ$, $[\alpha]_D - 74.34^\circ$, $[\alpha]_E - 96.77^\circ$, and $[\alpha]_F - 119.97^\circ$ at 22° in acetone ($c = 7.80$). The *l*-menthylurethane of ethyl *l*-tartrate has $[\alpha]_C - 31.04^\circ$, $[\alpha]_D - 38.76^\circ$, $[\alpha]_E - 48.64^\circ$, and $[\alpha]_F - 57.44^\circ$ under similar conditions ($c = 6.48$). The *l*-menthylurethane of ethyl mesotartrate has $[\alpha]_C - 45.14^\circ$, $[\alpha]_D - 57.78^\circ$, $[\alpha]_E - 74.16^\circ$, and $[\alpha]_F - 89.77^\circ$ ($c = 7.75$), values which are within 2 p.c. of those calculated by van't Hoff's principle of optical superposition. The *dl*-fenchylurethane of ethyl *d*-tartrate has $[\alpha]_C - 27.41^\circ$ (-35.59°), $[\alpha]_D - 35.29^\circ$ (-45.40°), $[\alpha]_E - 46.76^\circ$ (-59.47°), and $[\alpha]_F - 58.58^\circ$ (-74.01°) at 21° in acetone ($c = 5.58$) and chloroform ($c = 4.23$), the rotatory powers in brackets being those in the latter solvent. The *dl*-fenchylurethane of ethyl *l*-tartrate has $[\alpha]_C + 5.82^\circ$ (1.03°), $[\alpha]_D + 7.80^\circ$ (1.91°), $[\alpha]_E + 11.25^\circ$ (3.53°), and $[\alpha]_F + 13.52^\circ$ (5.59°) in acetone ($c = 4.809$) and chloroform ($c = 3.397$) at 21° . The *dl*-fenchylurethane of ethyl mesotartrate has $[\alpha]_C - 11.24^\circ$ (-16.51°), $[\alpha]_D - 14.35^\circ$ (-20.63°), $[\alpha]_E - 18.80^\circ$ (-26.41°),

and $[\alpha]_F - 23.07^\circ (-32.74^\circ)$ in acetone ($c = 5.159$) and chloroform ($c = 3.64$) at 21° ; these values are within 6 p.c. of those calculated by the principle of optical superposition. Tschugaev and Glebko (Ber. 1913, 46, 2752) assert, therefore, that the principle is tenable, at least as a first approximation (cf. Patterson, Chem. Soc. Trans. 1905, 87, 40; 1906, 89, 1884; 1907, 91, 705). The calculated values of the rotation dispersion-coefficients $[\alpha]_F/[\alpha]_C$ of the two urethanes of the mesotartrate agree exactly with those actually observed. The results also show that the abnormally high values of the dispersion-coefficients of the fenchylurethane of ethyl *l*-tartrate are caused by the superposition of the individual optical effects, thus confirming the view expressed (Chem. Soc. Abstr. 1911, ii. 787) that a relation exists between abnormal rotation dispersion and optical superposition of the partial rotations corresponding with the individual centres of optical activity (Chem. Soc. Abstr. 1913, ii. 897).

Methyl hydrogen tartrate $C_4H_5O_6 \cdot CH_3$ is prepared by boiling methyl alcohol (1 mol.) with tartaric acid (1 mol.). It forms rhombic crystals containing $1H_2O$, m.p. 76° (Tannhäuser, Zeitsch. Kryst. Min. 1908, 45, 183; Marckwald and Karczag, Ber. 1909, 42, 1518). For rotatory dispersion, see Lowry and Abram, Chem. Soc. Trans. 1915, 107, 1187; *ibid.* Abstr. ii. 660; Clough, *ibid.* 1915, 107, 96). For the alkaline hydrolysis, see Skrabal and Singer (Chem. Soc. Abstr. 1920, ii. 239). For acetyl derivative, see Freudenberg and Brauns (*ibid.* 1922, i. 623).

Ethyl hydrogen tartrate $C_4H_5O_6 \cdot C_2H_5$ is prepared by dissolving tartaric acid in an equal quantity of absolute alcohol in a retort at 60° – 70° , diluting with water and crystallising the product. It forms rhombic prisms, m.p. 90° (Guerin, *l.c.*).

o-Aminophenol tartrate $C_{16}H_{20}O_8N_2$, small white needles, loses water at 180° , yielding the compound



The acid tartrate of *m*-aminophenol



forms white needles (175° decomp.); the para-isomeride is converted at 180° – 200° into *p*-hydroxy-tartranil, slender white asbestos-like needles. Benzyl tartrate is a viscid yellow oil, obtained by heating benzyl alcohol and tartaric acid with potassium hydrogen sulphate at 130° (Medinger, J. pr. Chem. 1913, [ii.] 86, 345).

p-Aminophenol hydrogen ester.—See Casale (Chem. Soc. Abstr. 1918, i. 535).

n-Butyl tartrate melts at 22° and boils at $178^\circ/12$ mm.

For the rotation-dispersion of butyl tartrate, see Frankland and Garner (Chem. Soc. Trans. 1919, 636).

n-Heptyl tartrate $C_{18}H_{34}O_6$ melts at 35° – 35.5° and boils at $228^\circ/12$ mm.

For the rotation-dispersion of heptyl tartrate, see Frankland and Garner (Chem. Soc. Trans. 1919, 636).

n-Octyl tartrate $C_{20}H_{38}O_6$ melts at 41° – 42° and boils at $252^\circ/16$ mm.

For the rotation-dispersion of octyl tartrate,

see Frankland and Garner (Chem. Soc. Trans. 1919, 636).

p-Nitrobenzyl tartrate (Reid, Chem. Soc. Abstr. 1917, i. 334).

Phenacyl tartrate (Rather and Reid, Chem. Soc. Abstr. 1919, i. 158).

For the cinnamates of tartaric acid, see Erlenmeyer and Hilgendorff (*ibid.* 1917, i. 26).

For the amides and imides of tartaric acid, see Casale (*ibid.* 1917, i. 545, 643; 1918, i. 535).

For the azide and hydrazides of tartaric acid and their derivatives, see Curtius and Ohlgart (*ibid.* 1917, i. 638).

Di-l-menthylamine d-tartrate. For the rotation, see T. S. and D. C. Patterson (Chem. Soc. Trans. 1915, 150; *ibid.* Abstr. ii. 78).

Detection. Tartaric acid and tartrates char when heated, giving a smell resembling that of burnt sugar. Tartrates leave a residue consisting of the oxide or carbonate of the metal. Tartaric acid and tartrates char very readily when heated with strong sulphuric acid. To distinguish from citric acid or citrates, the substance is heated with pure concentrated sulphuric acid at 100° for 40 minutes. In the presence of tartaric acid the liquid becomes blackened, even as little as 1 p.c. in the substance treated giving a brown shade, whereas citric acid only imparts a yellow colour. For the detection of citric acid and tartaric acid, see Broeksmit (Chem. Soc. Abstr. 1917, ii. 429; see also Curtman and Harris (J. Amer. Chem. Soc. 1919, 41, 207).

With neutral solutions of tartrates calcium chloride gives a white crystalline precipitate of calcium tartrate. This precipitation only takes place after some time from dilute solutions and may be accelerated by scratching the sides of the containing vessel with a glass rod. If calcium acetate be used as the reagent, solutions containing 0.1 p.c. of tartaric acid give a precipitate, but by adding a few drops of *l*-tartaric acid or its ammonium salt a precipitate is formed in solutions containing only 0.0001 p.c. of tartaric acid, since calcium racemate is less soluble than calcium tartrate (Brönsted, Zeitsch. anal. Chem. 1903, 42, 15). For microscopical detection of calcium tartrate, v. Sullivan and Crampton, Amer. Chem. J. 1906, 36, 419.

Potassium acetate and acetic acid, when added to solutions of tartrates or of tartaric acid, yield a colourless precipitate of potassium hydrogen tartrate (de la Source, Compt. rend. 1895, 121, 774).

Silver nitrate gives with neutral solutions of tartrates a white precipitate of silver tartrate. A silver mirror is obtained by heating an ammoniacal solution of silver tartrate. The procedure is as follows: The silver tartrate is treated with ammonium hydroxide in a clean test-tube, until it is nearly all dissolved. A crystal of silver nitrate is placed in the bottom of the test-tube, which is then transferred to a beaker of boiling water. In a short time a silver mirror is produced on the sides of the tube.

If a few centigrams of resorcinol are heated with about 2 c.c. of concentrated sulphuric acid until vapours are evolved, and a small quantity of a tartrate is added, a bright-red coloration is produced. Or 2 grams of resorcinol may be dissolved in dilute sulphuric acid

(0.5 c.c. to 100 c.c. of water) and this used as the reagent. Two or 3 drops are added to 2 c.c. of concentrated sulphuric acid, and to this a very small quantity of the substance (liquid or solid). The solution is then heated at 115°–140° (Denigès, *J. Pharm. Chim.* 1895, [vi.] 1, 586; *Bull. Soc. chim.* 1909, [iv.] 5, 19; Mohler, *ibid.* 1890, [ii.] 4, 728). Tartaric acid gives a yellow, oxalic acid a green, and lactic acid a red coloration when heated with dilute sulphuric acid (1 : 1) and resorcinol (Brauer, *Chem. Zeit.* 1920, 44, 494). If pyrogallol is substituted for resorcinol, a violet-blue coloration is produced, whilst with β -naphthol the colour is blue in the cold, changing to an intense green on heating, and on dilution with 15–20 volumes of water, a permanent reddish-yellow colour is obtained (Piñerua, *Compt. rend.* 1897, 124, 291).

For the detection of tartaric acid in presence of formic and oxalic acids, *see* Krauss and Tampke (*Chem. Soc. Abstr.* 1921, ii. 466).

On adding a few drops of ferrous sulphate solution followed by a small quantity of hydrogen peroxide to a solution of a tartrate, a yellow coloration is produced, changing to violet on the addition of alkali hydroxide. The colour is discharged by acids and restored by alkalis (Fenton, *Chem. Soc. Proc.* 1893, 113).

If a few c.c. of cobalt nitrate solution be added to a solution of an alkali tartrate, a red colour is obtained which is discharged by alkali hydroxide. On boiling, a blue coloration is produced, which disappears on cooling and reappears on heating (Tocher, *Pharm. J.* 1906, 77, 87).

Another test consists in boiling the neutral solution with minium. After filtering, a few drops of a 2 p.c. solution of potassium thiocyanate are added. On standing the liquid darkens owing to a precipitation of lead sulphide. In testing wines a brownish-violet precipitate is obtained (Ganassini, *Boll. Chim. Farm.* 1903, 42, 513; Tagliavini, *ibid.* 1907, 46, 493).

For the detection of tartaric acid in wines, *see* Mathieu (*Chem. Soc. Abstr.* 1921, ii. 662).

A simple distinction between citric and tartaric acids has been found by H. Stevens (*J. Ind. Eng. Chem.* 1924, 16, 155). About 0.2 gm. of the sample is placed on a spatula and held in a flame until it ignites. The spatula is then removed and the ignition observed. In the case of tartaric acid the burning mass draws up into a dry ball and burns with a blue flame, the ball shrinking in size until only a small residue of carbon is left. The citric acid, when ignited, spreads out on the spatula, and remains in the liquid state while burning with a yellow flame; the burning is accompanied by considerable spluttering (*J. Soc. Chem. Ind.* 1924, 43, B. 277).

Estimation. Since all tartrates leave an oxide or carbonate on gentle ignition, they may be estimated by dissolving the residue in standard acid and determining the amount of acid thus neutralised with standard alkali.

For the estimation of free tartaric acid, alone or in the presence of citric acid, Allen recommends the following process (*Chem. News*, 1875, 31, 277): 2 grams of the sample are dissolved in 20 c.c. of proof spirit, and the filtered solution is diluted to 45 c.c. with proof spirit, treated with 5 c.c. of a cold saturated solution

of potassium acetate, and stirred for 10 minutes. The crystalline precipitate of potassium hydrogen tartrate is filtered off, washed with proof spirit, and, to remove any citrate carried down by the tartrate, is rinsed from the filter by a cold saturated solution of potassium hydrogen tartrate and digested therewith for a few hours. It is then again filtered, washed with proof spirit, rinsed with hot water into a weighed dish, and weighed after evaporating off the water at 100°. The precipitate may be dissolved and titrated with decinormal alkali and phenolphthalein instead of being weighed.

The higher results obtained by Teschmacher and Smith's modification of the Goldenberg method (*Chem. Soc. Abstr.* 1908, ii. 237) are probably due to the fact that the calcium carbonate is precipitated in an amorphous form; small quantities of potassium tartrate are liable to be precipitated with the crystallised calcium carbonate and removed with the latter from the solution (Perciabosco, *Chem. Zentr.* 1915, i. 1093; *Chem. Soc. Abstr.* 1915, ii. 595).

The addition of potassium acetate in the estimation of tartaric acid as potassium hydrogen tartrate does not entirely prevent a reversible reaction between tartaric acid and potassium chloride, and it also has a solvent action on the tartrate. Hartmann, Eoff, and Ingle (*Chem. Soc. Abstr.* 1916, ii. 400) recommend that, in the estimation of tartaric acid in wine, the latter should be neutralised with sodium hydroxide, a quantity of tartaric acid equivalent to the amount of alkali used then added, and glacial acetic acid next introduced, followed by the usual quantities of potassium chloride and alcohol. The mixture must be stirred until a precipitate is formed. After the precipitated potassium tartrate has been collected and titrated, the quantity of added tartaric acid is deducted from the result. The tartaric acid may also be added in the form of Rochelle salt. In dealing with synthetic solutions containing tartaric acid, phosphoric acid, and alcohol, it was found that esterification occurred gradually and that a preliminary saponification was necessary in order to obtain the whole of the tartaric acid.

Tartaric acid liquors.—These are the liquids obtained by the decomposition of calcium tartrate by sulphuric acid and are of a very complex nature. They contain free tartaric acid; other organic acids; sulphuric acid, and calcium, potassium, aluminium, and iron sulphates; phosphates and bodies of an indefinite nature. The analyst is usually required to estimate the tartaric acid, free sulphuric acid, and in some cases the total organic acids.

For the estimation of tartaric acid, potassium acetate is the best reagent for pure liquors, but cannot be used in the presence of iron or aluminium. In the latter case potassium citrate is used. A quantity of liquor containing 2–4 grams of tartaric acid (about 30–40 c.c.) is treated drop by drop with constant stirring with a saturated solution of potassium citrate until, the sulphuric acid having been converted into potassium sulphate, the citrate commences to react with the tartaric acid, which is precipitated as potassium hydrogen tartrate in streaks on the sides of the vessel. If much sulphuric acid is present a fine precipitate of potassium

sulphate precedes the appearance of the bitartrate. When the streaks begin to appear, a cubic centimetre of the citrate solution is added for every gram of tartaric acid supposed to be present, in all cases avoiding a great excess of the reagent. If a gelatinous precipitate should appear, the estimation is repeated with the previous addition of some citric acid. After stirring continuously for 10 minutes at a temperature not exceeding 15° , the precipitate is washed two or three times with 25 c.c. of a 5 p.c. solution of potassium chloride, saturated with potassium hydrogen tartrate. The precipitate is then collected on a small filter and washed with the same solution until the acidity of the filtrate is only slightly greater than that of the washing solution. The filter and precipitate are then transferred to a beaker and the amount of tartaric acid estimated by titration against standard alkali, phenolphthalein or litmus being used as an indicator. Sometimes a potassium hydrogen citrate is carried down with the tartrate and is difficult to separate. The best method is to dissolve the precipitate in 50 c.c. of hot water, add 5 grms. of potassium chloride, and cool the liquid quickly to 15° with continuous stirring for 10 minutes. This purified precipitate is then washed with the washing liquid and treated as above, but a correction of 0.5 p.c. must be added to the percentage of tartaric acid so found to allow for unavoidable losses in the purification process. From very old liquors containing much sulphuric acid potassium alum may be precipitated owing to its sparing solubility in solutions of potassium sulphate. To prevent this, phosphoric acid should be added before the citrate solution, and the liquid filtered immediately after stirring. For further details *v. Allen's Commercial Organic Analysis*, 1911, i. 541.

To estimate the free sulphuric acid, 20 c.c. of the liquid are made up to 200 c.c. with alcohol and allowed to remain overnight. The liquid is then filtered through a dry filter, and the alcohol evaporated from 100 c.c. of the filtrate. The sulphuric acid is then estimated as barium sulphate in the usual manner (Allen, *ibid.* 549).

To estimate the total organic acids, a known volume of the liquor is exactly neutralised with standard alkali and the liquid evaporated to dryness. The residue is ignited at a very low temperature until the carbon is nearly all burnt away. The ash is heated with a known volume of standard sulphuric acid, the solution decanted and the insoluble residue heated with more standard acid, concentrating the solution, if necessary, to dissolve the phosphates. To the mixed cold concentrated solutions, sufficient sodium potassium tartrate is added to keep any aluminium in solution and the solution titrated with standard alkali using litmus as an indicator. Each c.c. of normal sulphuric acid neutralised by the ash is equivalent to 0.075 gm. of organic acid, expressed in terms of tartaric acid (Warrington, *J. Chem. Soc.* 1876, 28, 982).

Estimation of tartaric acid volumetrically in presence of alkaline earth chlorides.—The fact that titration of alkali hydroxide against tartaric acid gives two end-points; that with helianthin indicating formation of the acid salt, and that with phenolphthalein the normal salt, may be used in estimating mixtures of tartaric acid

with other acids which give an end-point in presence of helianthin indicating the formation of normal salt. The presence of alkaline-earth chlorides in the solution introduces an error, as each molecule behaves towards potassium hydroxide as an equivalent quantity of hydrochloric acid. This effect is produced by any quantity and is quantitative in each case, the limiting value of the effect being the amount of tartaric acid present. Chlorides of other metals do not interfere with the titration in this manner (Simon and Zivy, *Compt. rend.* 1922, 175, 620; *Chem. Soc. Abstr.* ii. 1922, 880).

Lees, argols, and tartars.—About 8 grms. of the lees or argol (or 3 grms. of tartar) are heated on the water-bath with a little water for 5 minutes. Two grams of potassium oxalate are added and the mixture heated for a further 15 minutes. While hot the solution is nearly neutralised with a 3.5 p.c. solution of potassium hydroxide, the quantity of alkali being about 0.5 p.c. below that required for complete neutralisation, as determined by a preliminary experiment (*v. infra*). The solution is then heated on the water-bath for 30 minutes and the precipitate filtered off with the aid of a filter pump. The precipitate is washed ten times with water, using 3 c.c. each time, and the filtrate should have a volume of 50 c.c.; to this solution are added 5 grms. of potassium chloride and 2.5 grms. of citric acid, and after stirring continuously for 10 minutes, the solution is allowed to stand for 30 minutes. The precipitated potassium hydrogen tartrate is filtered off and washed with a 10 p.c. solution of potassium chloride saturated with potassium hydrogen tartrate, the acidity of which has been previously determined with *N/10* alkali. When the acidity of the washings is the same as that of the washing solution the precipitate is dissolved in hot water and titrated with *N/10* potassium hydroxide. The preliminary determination of the acidity of the sample is carried out as follows: Exactly 3 grms. of the sample are extracted with boiling water, the liquid decanted off and the operation repeated. The residue is transferred to a filter paper and washed until the washings are no longer acid. The solution is then titrated with 3.5 p.c. potassium hydroxide solution, using neutral litmus paper as an indicator (Allen, *ibid.* 546; Warrington, *l.c.*; Grosjean, *Chem. Soc. Trans.* 1879, 34).

Total tartaric acid.—Many methods have been proposed for the analysis of tartar and at the Seventh International Congress of Applied Chemistry, the method of Goldenberg, Geromont & Co. was adopted as being most suitable (*Zeitsch. anal. Chem.* 1908, 47, 57). A weighed amount of the sample (6 grms. if the tartaric acid yield is likely to be above 45 p.c.; 12 grms. if below that percentage) is digested with 18 c.c. of hydrochloric acid of sp. gr. 1.1 for 10 minutes. The whole mass is then washed into a 200 c.c. graduated flask, made up to the mark with distilled water, shaken well and filtered through a dry filter into a dry flask. 100 c.c. of the filtered liquid are then poured into a 300 c.c. beaker, containing 10 c.c. of potassium carbonate solution (66 grms. of pure carbonate in 100 c.c.). The solution is brought to boiling and kept at that point for 20 minutes until the calcium carbonate has separated in a crystalline form.

The liquid and precipitate are rinsed into a 200 c.c. flask, made up to the mark and filtered through a dry filter. 100 c.c. of the filtrate are transferred to a porcelain basin and evaporated to 15 c.c. While the liquid is still hot, 3.5 c.c. of glacial acetic acid are added gradually with constant stirring, which is maintained for 5 minutes after the acid has been added. After standing for 10 minutes, 10 c.c. of 95 p.c. alcohol are added and the liquid stirred for another 5 minutes. The liquid is allowed to stand for a further 10 minutes and then filtered with the aid of a pump and washed with alcohol until the washings are no longer acid (*v. infra*). The filter and precipitate are transferred by means of 200 c.c. of hot water into a porcelain basin, the liquid brought to boiling and titrated with *N*/5 alkali, using neutral litmus paper as the indicator. The alkali must have been standardised against pure potassium hydrogen tartrate, using the same paper as indicator. A correction has to be made since the volume of undissolved matter has not been allowed for in making the solution up to the various volumes. It was agreed that for samples containing less than 45 p.c. of acid, 0.8 should be deducted; for those containing from 45 p.c. to 60 p.c., 0.3; from 60 p.c. to 70 p.c., 0.2; and for those containing over 70 p.c. no deduction should be made. To control the washings 30 c.c. of the alcohol are titrated with standard alkali, using phenolphthalein as indicator. The washing is continued until 30 c.c. of the filtrate require the same amount of standard alkali to give the colour that was produced in the test with the original 30 c.c.

This method has been criticised by Heczko (Zeitsch. anal. Chem. 1911, 50, 12), Tobler and Caramelli (J. Soc. Chem. Ind. 1911, 207), Ordonneau (Bull. Soc. chim. 1910, [iv.] 7, 1034), and Beys (Compt. rend. 1910, 150, 1250; Bull. Soc. chim. 1910, [iv.] 7, 697), L. and J.

Gadais (Bull. Soc. chim. 1913, 13, 722). According to Carles (Ann. Chim. anal. 1917, 22, 71) the Goldenberg method sometimes gives low results when applied to crude tartars containing a large proportion of calcium tartrate; this is probably due to incomplete decomposition of the calcium tartrate during the treatment with potassium carbonate. It is recommended that the hydrochloric acid solution of the sample should be added gradually with constant stirring to the potassium carbonate solution, and the mixture then boiled until all hydrogen carbonates have been decomposed; the mixture should now be alkaline to phenolphthalein. The presence of undecomposed calcium tartrate is indicated if the separated and washed calcium carbonate is not completely soluble in acetic acid (Chem. Soc. Abstr. 1917, ii. 278). According to Heczko the results obtained are influenced by the amount of calcium salts present, as they are not completely precipitated by potassium carbonate in the presence of tartrates. Also the insolubility of potassium hydrogen tartrate depends on the temperature and concentration of the solution from which it is precipitated. Tobler and Caramelli state that the error introduced by making the solution up to 200 c.c. after treatment with potassium carbonate increases with the amount of precipitated calcium carbonate, and the suggested corrections do not adequately allow for it. Ordonneau has made a series of determinations by the Goldenberg method, using for the purpose of analysis pure potassium hydrogen tartrate and calcium tartrate to which known quantities of the impurities which occur in tartars were added. He concludes that the error when litmus is used as indicator is double that obtained with phenolphthalein and that the best results are obtained with the latter indicator at 50° after boiling and cooling to that temperature. His results are tabulated below:—

Impurities added to potassium hydrogen tartrate	Total tartaric acid	Percentage of impurity	Loss of tartaric acid		Loss of tartaric acid per gram of impurity	
			Litmus	Phenolphthalein	Litmus	Phenolphthalein
Calcium phosphate (tribasic)	75.80	5	2.35	1.60	0.47	0.32
Ferrous phosphate	75.80	5	6.15	3.68	1.22	0.73
Ferric phosphate	75.80	5	7.95	3.98	1.59	0.79
Aluminium phosphate	75.80	5	4.65	2.20	0.93	0.44
Alumina, pure anhydrous	75.80	5	19.35	8.80	3.87	1.76
Ferric chloride, dry (\equiv 4.92 grms Fe_2O_3)	71.81	10	13.38	7.21	2.71	1.46
Calcium tartrate	78.69	5	1.77	0.99	—	—
Calcium tartrate	77.57	10	1.85	1.04	—	—
Calcium tartrate (alone)	57.69	—	2.08	2.00	—	—

Tartaric acid may be estimated in tartrates, esters, and wines by precipitation as calcium racemate. To the solution of the tartrate (which in natural products is always dextro-rotatory) is added a sufficiency of lævo-rotatory alkali tartrate, thus forming a racemate which is then precipitated by addition of calcium acetate. The precipitate is washed with cold water and dissolved in boiling 4 p.c. hydrochloric

acid, from which it is then reprecipitated by boiling with an excess of acid sodium and calcium acetate; any lævo-rotatory calcium tartrate contained in the racemate is thus got rid of. When cold the precipitate is washed and dissolved in boiling dilute sulphuric acid, and, while boiling, titrated with standard potassium permanganate, which has been checked against tartaric acid. The result is divided by two

(Kling, Bull. Assoc. chim. Sucr. Dist. 1911, 28, 893). For the estimation of tartaric acid, the process by precipitation as calcium racemate (Chem. Soc. Abstr. 1911, ii. 666) is again recommended. If tartaric esters are also present, the total amount of the tartaric acid may be estimated after saponification. If ethyl hydrogen tartrate is present, the tartaric acid contained therein may be estimated by titration, allowance being made for any free tartaric acid. The result must then be multiplied by two.

According to Astruc (Ann. Falsif. 1914, 7, 416) the racemate method (Chem. Soc. Abstr. 1910, i. 651; ii. 359; 1911, ii. 666) for the estimation of potassium hydrogen tartrate and tartaric acid is recommended as being trustworthy (Chem. Soc. Abstr. 1915, ii. 112; Kling and Gelin, 8th Inter. Cong. App. Chem. 1912, 1, 251; Chem. Soc. Abstr. 1913, ii. 737).

In the quantitative oxidation of dilute solutions of tartaric acid by potassium permanganate in the presence of a sufficient quantity of sulphuric acid, no precipitate of manganese dioxide is formed, so that addition of excess of oxalic acid and back titration are unnecessary. The permanganate solution should be standardised with pure potassium hydrogen tartrate. The latter, when crude, contains organic impurities, and cannot be directly titrated with permanganate. It should first be separated by precipitation from alcoholic solution. The oxidation of tartaric acid by hydrogen peroxide in the presence of an iron salt or, better, of a copper salt, finds application in both qualitative and quantitative analyses (e.g. determination of iron and aluminium in presence of each other, etc.) (W. Meigen and I. Schnerb, Zeitsch. angew. Chem. 1924, 37, 208; J. Soc. Chem. Ind. 1924, 43, B. 574).

Optical methods for the estimation of malic and tartaric acids in the same solutions.—According to Willaman (J. Amer. Chem. Soc.) one method depends on the facts that uranyl acetate enhances the rotation of *l*-malic and *d*-tartaric acids, whilst ammonium heptamolybdate reverses the direction of the rotation in the case of *l*-malic acid, giving strongly positive solutions in each case. A chart is made connecting the rotations of solutions, containing up to 1 p.c. of the acids, activated by uranyl acetate on the one hand (the curves slope down from left to right) with those of solutions activated by ammonium heptamolybdate on the other (the curves slope up from left to right). The point of intersection of a given pair of curves will give, therefore, the number of grams of tartaric acid on the abscissæ and the proportion of malic acid on the ordinates.

The details of the method are based on Goder's work on malic acid (Chem. Soc. Abstr. 1911, ii. 1141), and further developments by Gore and others in America, which have been embodied in an official process (J. Assoc. Off. Agric. Chemists, 1916). An amount of the sample is taken which, judged by titration, will contain at least about 0.1 gm. of either acid and not more than 0.6 gm. of tartaric acid or 0.8 gm. of malic acid. This is neutralised with *N*-ammonia solution, mixed with 2 vols. of 95 p.c. alcohol, filtered from pectins, and the filtrate slowly mixed with an excess of a 10 p.c.

solution of barium chloride in 50 p.c. alcohol, and then made up to fourteen times the original volume with 95 p.c. alcohol. The precipitate is collected by centrifuging, boiled with water, mixed with 10 c.c. of 20 p.c. ammonium sulphate solution, the mixture is concentrated to about 80 c.c., cooled, mixed with 6 c.c. of glacial acetic acid, and diluted to 100 c.c. Two 25 c.c. portions of the clear solution, after centrifuging, are taken, mixed with 10 c.c. of an 8 p.c. solution of pure uranyl acetate and 10 c.c. of 10 p.c. ammonium heptamolybdate respectively, left for three hours in the dark, and then polarised at about 20° in a 2-dcm. tube. If the molybdate solution becomes green through reduction, a drop of bromine water may be added (Chem. Soc. Abstr. 1918, ii. 249).

It has been shown by Dunbar and Bacon (Chem. Soc. Abstr. 1912, ii. 699) that malic acid can be estimated by measuring the increase in rotation produced by treating the solution with uranyl acetate. It was pointed out that the specific rotation of *d*-tartaric acid is also increased by uranium salts, and that the presence of this acid therefore interferes with the estimation of malic acid. The present work was undertaken with the object of devising a method for estimating tartaric acid, and which could be applied to the estimation of both malic and tartaric acids in the same solution. In this paper an account is given of a method for estimating tartaric acid. If a solution of tartaric acid or tartrates from 0.2 to 3.0 grms. of the acid per 100 c.c. is treated with uranyl acetate, each gram of acid in 100 c.c. produces a rotation of +19.6°, the ratio of tartaric acid concentration to rotation being 0.051. Hence, in the absence of malic acid, tartaric acid can be estimated by treating the solution with uranyl acetate, polarising, and multiplying the reading by 0.051. In presence of other optically active substances, a portion of the solution must be freed from tartaric acid by precipitation with lead acetate and polarised separately. The difference between this reading and that obtained with the solution treated with uranyl acetate gives the polarisation due to the uranyl tartaric complex (Dunbar, Eighth Inter. Cong. App. Chem. 1912, 26, 361; Chem. Soc. Abstr. 1913, ii. 801).

A method has now been devised by Dunbar (Eighth Inter. Cong. App. Chem. 1912, 26, 375; Chem. Soc. Abstr. 1913, ii. 802) for estimating both acids in the same solution, which is based on the facts: (1) that the rotations of both acids are increased independently by treatment with uranyl acetate under definite conditions, and (2) that both acids can be oxidised quantitatively to oxalic acid by heating with potassium permanganate in alkaline solution. When determinations have been made of the total rotation produced on addition of uranyl acetate, and the amount of oxalic acid formed on oxidation or the quantity of permanganate reduced, the amounts of malic and tartaric acids present can be calculated. The method is interfered with by the presence of substances which form oxalic acid on oxidation, and which cannot be removed before treatment with the permanganate.

The following procedure is recommended for the estimation of tartaric, malic, and citric

acids: (1) Separation of the mixed acids by the process described by Mestrezat (Chem. Soc. Abstr. 1906, ii. 635), and estimation of the lactic acid by Moeslinger's method. (2) Estimation of the tartaric acid by Kling's method (Chem. Soc. Abstr. 1912, ii. 1006). (3) Oxidation of the mixture of the three acids by permanganate in both acid and alkaline solution. In acid solution, 1 grm. of potassium permanganate oxidises 1.447 grms. of tartaric acid, 2.078 grms. of malic acid, or 1.820 grms. of citric acid, whilst in alkaline solution the same quantity of permanganate oxidises 0.620 grm. of tartaric acid, 0.615 grm. of malic acid, or 0.380 grm. of citric acid (Mathieu and Ferre, Chem. Soc. Abstr. 1914, ii. 990).

According to Dean (Chem. News, 1915, 112, 154), tartaric acid may be titrated with permanganate by the following method: The solution of tartrates is acidified with 3 c.c. of nitric acid, and titrated to a permanent pink. The solution is then neutralised, zinc nitrate is added, and the whole is titrated, boiling, with permanganate, as in the Volhard method. Under these conditions the tartaric acid is oxidised completely to carbon dioxide and water, and fairly accurate results may be obtained. The oxidation in acid solution only required about two-thirds of the permanganate which would be necessary for the complete oxidation, and some tests indicated that the intermediate compound was formic acid, which was further oxidised during the second part of the titration in neutral solution (Chem. Soc. Abstr. 1915, ii. 804).

Lead in tartaric acid.—The following method is due to W. A. Davis (Allen's Commercial Organic Analysis, 1911, i. 550, 569; cf. Wilkie, J. Soc. Chem. Ind. 1909, 28, 637). The reagent is freshly prepared colourless ammonium sulphide, obtained by diluting 2 c.c. of 0.880 ammonia to 10 c.c. and saturating with well-washed hydrogen sulphide. Standard lead solutions are made by dissolving 5 grams of pure lead in nitric acid, evaporating to remove all but the last traces of nitric acid and diluting to 1000 c.c. For use portions of it are taken, diluted 100 times and treated in the usual manner for colour comparisons.

Ten grams of tartaric acid are dissolved in 25 c.c. of hot water, cooled, and to the solution are added 2 c.c. of *N*/10 sodium thiosulphate solution. The solution is heated nearly to boiling, cooled, and 1 c.c. of a 10 p.c. solution of potassium cyanide is added. Then ammonia (0.880) is added until the liquid has a faint smell of the reagent. The liquid is boiled until it is colourless, poured into a tall cylinder, made up to 100 c.c. and treated with 2 drops of the freshly prepared reagent. The tint obtained is compared with tints produced by solutions made from pure lead-free tartaric acid to which known amounts of the lead nitrate solution have been added, so as to give comparisons of the order of 5 parts per 1,000,000, 10 parts per 1,000,000, &c. If it is desired to test cream of tartar, 10 grams should be dissolved in hydrochloric acid and after the addition of sodium thiosulphate, the above method can be used.

R. L. Andrew has described a method for the colorimetric estimation of lead in cream of tartar. It is found to be less cumbersome than

the B.P. method. One c.c. of 5 p.c. potassium cyanide solution, 1 c.c. of ammonia solution, and 40 c.c. of water are added to 2 grms. of cream of tartar, and solution effected by warming and shaking. After cooling and filtering, any tint is matched in the standards by the addition of very dilute caramel. These standards are prepared in a similar way from 2 grms. of lead-free cream of tartar, with the addition of requisite amounts of lead nitrate solution containing 0.01 p.c. of lead. A few drops of 10 p.c. sodium sulphide solution are added and the amount of lead estimated by comparison. If a standard aqueous solution of lead is used a serious error is introduced, as the colour is only about half the depth of that produced with a tartrate solution (J. Soc. Chem. Ind. 1923, 42, 1211).

Wines.—A method for the detection of free tartaric acid in wines may be based upon its partial extraction with amyl alcohol, in which potassium hydrogen tartrate and calcium tartrate are insoluble. For estimating tartaric acid in wines the method of Kling may be used (Compt. rend. 1910, 150, 616; Bull. Soc. chim. 1912, [iv.] 11, 886). 25 c.c. of the solution, diluted or concentrated so as to contain 3–4 grms. of tartaric acid per litre, are added to 100 c.c. of water. To the solution are added 25 c.c. of a solution of *l*-potassium sodium tartrate (16 grms. per litre) and 20 c.c. of a solution of calcium acetate (30 grms. per litre). The precipitated calcium racemate is filtered off, washed, and dissolved in 20 c.c. of hydrochloric acid (40 grms. per litre). The solution is diluted to 150 c.c. and 40 c.c. of a solution of sodium acetate 10 p.c.) and calcium acetate (1 p.c.) is added and the liquid heated to boiling. After cooling, the racemate is collected, washed, dissolved in boiling dilute sulphuric acid and titrated at the boiling-point with potassium permanganate solution (16 grms. per litre), which has been standardised against potassium hydrogen tartrate. In the presence of considerable amounts of iron or aluminium salts, &c., the initial precipitation must be performed in the presence of ammonium citrate (Kling and Florentin, Ann. Falsif. 1912, 5, 518, cf. p. 695). According to M. François and C. Lormand (J. Pharm. Chim. 1923, [vii.] 28, 433), in Kling's method for determining tartaric acid in wine (cf. A. 1910, ii. 359), which depends on the precipitation of the very insoluble calcium racemate by addition of *l*-tartaric acid in excess and calcium acetate, incorrect results are liable to be obtained on account of the sparing solubility of calcium *l*-tartrate. The present authors find the solubility of the calcium tartrates in water at 20° to be: calcium *d*-tartrate and calcium *l*-tartrate, both $C_4H_4O_6Ca, 4H_2O$, 0.232 and 0.149 grm. per litre, respectively; calcium racemate, 0.0493 grm. per litre. The solubility of the *d*-tartrate in alcohol of 32 vol. p.c. strength is, however, sufficiently small (0.038 grm. per litre, at 20°) to allow of the direct determination of tartaric acid by precipitation of this salt. The sample for analysis should contain about 0.4–0.6 grm. of tartaric acid, and is made up to 100 c.c. with water. To this solution is added 20 c.c. of a solution of calcium acetate (32 grms. of pure calcium carbonate and 120 c.c. of glacial acetic acid, made up to 1 litre with water), and then, after stirring, 30 c.c. of alcohol of 95 vol. p.c.

strength. After keeping the mixture for 24 hours, a further 30 c.c. of the alcohol is added. After a further 24 hours, the crystals of calcium *d*-tartrate are collected, preferably in a Gooch crucible, dried in the air at room temperature and weighed. The results are accurate to about 1 p.c. The characteristic appearance of the crystals of calcium *d*-tartrate may be used for the detection (Chem. Soc. Abstr. 1924, 126, ii. 129). For other methods of estimation in wines, *v.* Gowing-Scopes, *Analyst*, 1908, 33, 315; von Florentz, *Chem. Zeit.* 1907, 31, 1118; Malvezin, *Bull. Soc. chim.* 1912, [iv.] 11, 1043; Baragiola, *Chem. Zentr.* 1913, ii. 179; Dutoit and Duboux, *Bull. Soc. chim.* 1913, [iv.] 13, 832; Duboux, *Ann. Chim. anal.* 1914, 19, 89; Kling and Lassieur, *Ann. Falsif.* 1914, 7, 410; Häussler, *Zeitsch. anal. Chem.* 1914, 53, 542; Hartmann, Eoff, and Ingle, *J. Ind. Eng. Chem.* 1916, 8, 422; Kunz, *Chem. Zentr.* 1915, ii. 287; Carles, *Ann. Chim. anal.* 1915, 22, 240; *v.* also article on WINE, vol. vii.

L-TARTARIC ACID.

This acid, which has also been called *anti-tartaric acid*, was first obtained by Pasteur (*Ann. Chim.* 1850, [iii.] 28, 56) by the crystallisation of a solution of sodium ammonium racemate. The product was found to consist of a mixture of hemihedral crystals, some having the hemihedral faces developed to the right and others to the left, the former being dextro-rotatory, and the latter lævo-rotatory. The acid obtained from the former was *d*-tartaric acid, while the latter yielded a lævo-rotatory acid, *l*-tartaric acid (*cf.* Bichat, *Bull. Soc. chim.* 1886, [ii.] 46, 54; Jungfleisch, *J.* 1883, 1084). The best method of preparation is that due to Marckwald (*Ber.* 1896, 29, 42; *cf.* Kling, *Bull. Soc. chim.* 1910, [iv.] 7, 774). To a boiling aqueous solution of racemic acid is added gradually half the amount of cinchonine necessary to form the acid salt and sufficient water to give a clear solution. After standing for one day cinchonine *l*-tartrate crystallises out, from which *l*-tartaric acid can be obtained in the usual manner. The yield is two-thirds of that demanded by theory. For asymmetric synthesis by the action of potassium permanganate on *l*-bornyl fumarate, *v.* McKenzie and Wren, *Chem. Soc. Trans.* 1907, 1215.

Properties.—*l*-Tartaric acid forms anhydrous rhombic crystals, m.p. 168°–170° (Bischoff and Walden, *Ber.* 1889, 22, 1820; *Zeitsch. physikal. Chem.* 1891, 8, 466). It resembles *d*-tartaric acid in most of its physical properties (*v.* p. 678), but the two acids are oppositely pyroelectric and also solutions of the same concentration rotate the plane of polarised light an equal amount, but in opposite directions. Solutions of *l*-tartaric acid are destroyed by *Schizomycetes*. The salts of *l*-tartaric acid have the same number of molecules of water of crystallisation and the same crystalline form as those of *d*-tartaric acid. They exhibit opposite hemihedry, opposite rotation and are oppositely pyroelectric. They are also somewhat more soluble than the corresponding salts of the *d*-acid (Jungfleisch, *Bull. Soc. chim.* 1884, [ii.] 41, 223). There are differences between the compounds of the two acids with optically

active substances. Thus a partially racemic compound is obtained by the combination of ammonium *d*-tartrate and ammonium *l*-malate, whilst ammonium *l*-tartrate does not undergo this combination (*v.* RACEMISM). The compounds with optically active bases also are different, thus cinchonine *d*-tartrate crystallises with 4H₂O, whilst the *l*-salt only has 1H₂O, but the affinity constants of *d*- and *l*-tartaric acids for optically active bases are the same (Marckwald and Chwolle, *Ber.* 1898, 31, 783).

RACEMIC ACID.

This acid, which is also known as *r*-tartaric acid or *paratartaric acid*, was discovered by Kestner in the mother-liquors of tartaric acid obtained from the vintage of 1822 (*Compt. rend.* 1849, 29, 526, 557), and was examined by Gay-Lussac (*Schweigger's J.* 48, 381), Walchner (*ibid.* 49, 238), Berzelius (*Pogg. Annalen*, 19, 319), and Biot (*Ann. Chim.* [ii.] 69, 22), of whom the last-named pointed out its optical inactivity. Pasteur investigated its properties further and decomposed it into *d*- and *l*-tartaric acids (*Compt. rend.* 1853, 36, 19; 37, 162). Racemic acid appears to exist to some extent in grape juice, but is produced chiefly during the fermentation. It is produced to a certain extent in the tartaric acid works in the process of purification, and after crystallising cream of tartar, potassium ammonium racemate can be extracted from the mother-liquors.

For the resolution of *r*-tartaric acid by means of *l*-borneol and its bornyl esters, *see* Wren, Williams, and Myddleton (*Chem. Soc. Trans.* 1920, 191).

Preparation. Most methods for the production of racemic acid result also in the formation of *mesotartaric acid*, from which it may be separated by the method given on p. 679. The following are the chief methods for the interconversion of the tartaric acids. When *d*-tartaric acid is heated for 30 hours at 170° with one-seventh to one-tenth of its weight of water, racemic acid is the main product, whilst by heating *d*-tartaric acid (or racemic acid) (30 grms.) with 4 c.c. of water for 2 days at 165°, *mesotartaric acid* is produced (Jungfleisch, *Bull. Soc. chim.* 1872, [ii.] 18, 203; 1873, [ii.] 19, 101; 1874, [ii.] 21, 146; 1878, [ii.] 30, 191; *cf.* Dessaignes, *ibid.* 1863, [i.] 5, 356). According to Meisner, the yield of *mesotartaric acid* is only 5.5 p.c. by this method, and if 100 grms. of *d*-tartaric acid are heated with 350 grms. of sodium hydroxide, and 700 grms. of water during 8 hours in a copper flask, racemic acid is obtained almost free from *mesotartaric acid*, only 1.3 p.c. of the latter being produced (*Ber.* 1897, 30, 1574). Holleman states that by heating *d*-tartaric acid for 8 hours with boiling alkali, 25 p.c. of *mesotartaric acid* is produced, the maximum yield of 31 p.c. being obtained after only 2 hours' heating (*Rec. trav. chim.* 1898, 17, 66; *cf.* Bosekin, *ibid.* 224). Holleman also heated 6 grms. of *d*-, *r*-, and *i*-tartaric acids with 4 c.c. of *N*-hydrochloric acid in sealed tubes and obtained the following results. *d*-Tartaric acid below 140° yielded *i*-tartaric acid almost entirely, but after 42 hours at 155°, 6.7 p.c. of *r*-tartaric acid and 18 p.c. of *i*-tartaric acid were obtained. *r*-Tartaric acid, after 100

hours at 140°, yielded 19 p.c. of *i*-tartaric acid, and the latter under similar conditions gave 10 p.c. of the *r*-tartaric acid. Finally, when *d*- and *l*-tartaric acids are mixed in equal quantities in solution, racemic acid is the sole product.

By heating dibromosuccinic acid or isodibromosuccinic acid with 200 parts of water, a mixture of mesotartaric and racemic acids is obtained, the former yielding chiefly mesotartaric acid and the latter racemic acid (Lossen and Riebensahm, *Annalen*, 1896, 292, 295; cf. Pasteur, *Annalen*, Suppl. 2, 242). A similar result is obtained by using the silver salt (Perkin and Duppa, *Quart. J. Chem. Soc.* 1861, 13, 112; Kekulé, *Annalen*, 1860, 117, 121). By heating an alcoholic solution of glyoxal with a 5 p.c. excess of alcoholic hydrocyanic acid, a mixture of the nitriles of racemic and mesotartaric acids is produced (Pollak, *Monatsh.* 1894, 15, 469; Strecker, *Zeitsch. Chem.* 1868, 216; Schöyen, *Annalen*, 1864, 132, 168; Staedel, *Ber.* 1878, 11, 752). When phenol is oxidised with potassium permanganate in alkaline solution a mixture of *r*- and *i*-tartaric acids is obtained (Doebner, *Ber.* 1891, 24, 1755).

Racemic acid may be obtained by reducing glyoxylic acid with zinc and acetic acid, glycollic acid also being produced (Genvresse, *Compt. rend.* 1892, 114, 555); by oxidising fumaric acid with potassium permanganate (Kekulé and Anschütz, *Ber.* 1880, 13, 2150; *Annalen*, 1884, 226, 191; cf. Tanatar, *Ber.* 1879, 12, 2293); by treating piperic or sorbic acid with dilute potassium permanganate solution (Doebner, *ibid.* 1890, 23, 2374); by the action of nitric acid on fructose, mucic acid, and inulin, the first-named also yielding mesotartaric acid (Kiliani, *ibid.* 1881, 14, 2530); and together with *d*-tartaric acid by the action of nitric acid on dulcitol, mannitol, milk sugar, cane sugar, and saccharic acid (Carlet, *J.* 1860, 249; 1861, 367; Hornemann, *J. pr. Chem.* 1861, [i.] 89, 283).

Carbon monoxide and an alkali hydroxide combine at 180°–220° to give a formate which yields the corresponding oxalate when heated to 360°–440° under pressure. This can be reduced by an amalgam in presence of acid to a glyoxalate which yields racemic and mesotartaric acids on electrolytic reduction in alkaline solution (Baekeland and Peter, *J. Soc. Chem. Ind.* 1916, 944).

Properties. Racemic acid crystallises in large plates belonging to the triclinic system and which contain 1 mol. of water of crystallisation. It is less soluble in water or alcohol than tartaric acid, and has m.p. 205°–206°; sp.gr. 1.697 (Walden, *Ber.* 1896, 29, 1701). The reactions which it undergoes are the same as those of tartaric acid.

The racemates resemble the tartrates in most respects, but differ in their solubility and in the number of molecules of water of crystallisation which they contain. As a rule (barium tartrate being the only known exception) the salts of inactive tartaric acid are invariably less soluble in water than those of the active form. (For a series of determinations of solubilities, see Duboux and Cuttat, *Helv. Chim. Acta*, 1921, 4, 735.) Thus *potassium racemate* crystallises in the rhombic system with 1H₂O, or in the monoclinic with 2H₂O (van't Hoff and Müller, *Ber.* 1899, 32, 857), whilst the *rubidium salt* crystal-

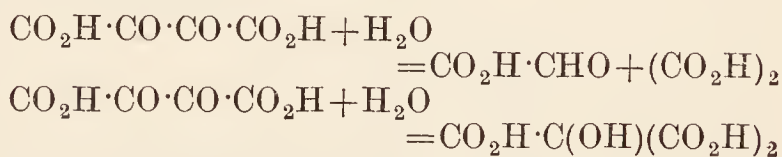
lises in the monoclinic system with 2H₂O at low temperatures; at higher temperatures the solution deposits crystals of rubidium *d*- and *l*-tartrates (Traube, *Sitzungsber. Berl. Akad.* 1895, 10, 195; Wyrouboff, *Chem. Zentr.* 1901, ii. 764; cf. van't Hoff and Müller, *Ber.* 1898, 31, 2206). *Calcium racemate* crystallises in fine needles containing 4H₂O, and is obtained by adding calcium sulphate to a soluble racemate or racemic acid. It is even less soluble than calcium tartrate, and use is made of this fact in Kling's method for the estimation of tartaric acid (*v. p.* 695). For distinction from calcium tartrate *v. pp.* 690, 692. Calcium is better estimated in water as racemate than as oxalate, since magnesium does not then affect the results. The *barium salt* crystallises with 2½H₂O and with 5H₂O (Lossen and Riebensahm, *Annalen*, 1896, 292, 313; Mügge, *Chem. Zentr.* 1899, ii. 245). For resolution of racemates into *d*- and *l*-tartrates, *v.* RACEMISM.

For the crystalline structure of anhydrous racemic acid, see W. T. Astbury, *Proc. Roy. Soc. A*, 104, 1923, 219.

For the active racemic compound of tartaric acid, see Landriew (*Chem. Soc. Abstr.* 1922, i. 808).

DIHYDROXYTARTARIC ACID.

Dihydroxytartaric acid, considered as a diketone, has a structure similar to benzil, and when acted on by alkalis behaves like benzil, and thus its decomposition is represented by the equations



the carboxytartronic acid losing carbon dioxide and giving tartronic acid. It is shown that when sodium dihydroxytartrate is heated at 160°, carbon dioxide is evolved and glyoxylic acid and oxalic acid were identified along with tartronic acid in the products of decomposition.

In Fenton's method for the estimation of sodium by precipitation as sodium dihydroxytartrate and subsequent oxidation of this salt with standard permanganate, it is necessary to carry out the oxidation first in alkaline and then in acid solution in order to obtain consistent results (Lachman, *J. Amer. Chem. Soc.* 1921, 43, 2091; cf. Fenton, *Chem. Soc. Trans.* 1898, 74, 71; 1902, 81, 426; *Chem. Soc. Abstr.* 1922, i. 109).

NITROTARTARIC ACID.

Nitrotartaric acid, of which the preparation is detailed, is stable at the boiling-point of xylene after careful dehydration over lime or sodium hydroxide, but slowly decomposes in presence of water into nitrous and dihydroxytartaric acids, with some tartronic and oxalic acids, whilst the last two are the only organic acids produced in presence of alkali. It is suggested that these reactions are not due to methylene dissociation (Nef, *Chem. Soc. Abstr.* 1900, i. 4), but to a pseudo-form of the acid, CO₂H·C(OH)(ONO)·C(OH)(ONO)·CO₂H. The acid itself is the dinitrate of tartaric acid, CO₂H·CH(ONO₂)·CH(ONO₂)·CO₂H, since it yields tartaric and nitric acids on hydrolysis at

the ordinary temperature by concentrated hydrochloric acid, or by moderately dilute sulphuric or nitric acid (Lachman, J. Amer. Chem. Soc. 1921, 43, 577; Chem. Soc. Abstr. 1921, i. 303).

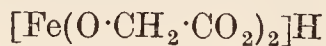
TARTRATOFERRIC ACID.

According to Paira the compounds described are analogous in constitution to the salts of salicylatoferric acid prepared by Weinland (Chem. Soc. Abstr. 1913, i. 1189). *Potassium diglycollatoferrate*



is obtained as an apple-green precipitate when very concentrated solutions of ferric chloride and potassium glycollate are mixed; from dilute solutions the salt is precipitated by means of alcohol. The corresponding *sodium* salt has $1\frac{1}{2}\text{H}_2\text{O}$ of crystallisation.

When a mixture of ferric hydroxide (1 mol.) and glycollic acid (6 mols.) is kept cold and in the dark for a long time, a microcrystalline, green powder of diglycollatoferric acid



is obtained; it is readily decomposed by water and liberates carbon dioxide from carbonates.

By the addition of sodium carbonate (0.5 mol.) to a solution of ferric chloride (1 mol.), a yellow, sparingly soluble precipitate of *tartrato-ferric acid* ($\text{C}_4\text{H}_2\text{O}_6\text{Fe}$)H is obtained, which is readily soluble in alkalis; it is also obtained by the interaction of ferric hydroxide and tartaric acid. The *sodium* and *potassium tartratoferrates* ($\text{C}_4\text{H}_2\text{O}_6\text{Fe}$)Na, $5\text{H}_2\text{O}$ and



are obtained either from the free acid and the appropriate alkali, or from ferric chloride and the alkali tartrates. They are very soluble in water, but can be recrystallised from dilute alcohol. Concentrated solutions, when dried on a glass plate, give large, brownish-yellow scales (Chem. Soc. Abstr. 1914, i. 1123).

MesOTARTARIC ACID.

Mesotartaric acid, which is also known as *i-tartaric acid*, was first obtained by Pasteur, together with racemic acid, by heating cinchonine *d*- or *l*-tartrate for some time at 170° . Most of the methods of preparation result also in the production of racemic acid, the best being that of Holleman (*v. Racemic acid*). It may also be obtained by treating *mesodiaminosuccinic acid* with nitrous acid (Farchy and Tafel, Ber. 1893, 26, 1986; *cf.* Lehrfeld, *ibid.* 1881, 14, 1819), or by oxidising sorbinose (Dessaignes, Annalen, Suppl. 2, 242), erythritol (Przybtek, J. Russ. Phys. Chem. Soc. 1880, 12, 209) or glycerol (*ibid.* 1881, 13, 330) with dilute nitric acid.

It crystallises in rectangular plates containing 1 mol. of water of crystallisation, and has m.p. 140° and sp.gr. 1.666 (Bischoff and Walden, Ber. 1896, 29, 1702). It is slightly less soluble in water than tartaric acid. Its affinity constant is 0.060. The *mesotartrates* resemble the tartrates except in their solubility and in the number of molecules of water of crystallisation which they contain. Thus the *calcium salt* contains $3\text{H}_2\text{O}$ and, like the potassium salt, is more soluble than the corresponding salt of tartaric acid. Marckwald and Karczag (Ber. 1909, 42, 1518) have prepared two optically

active methyl hydrogen *mesotartrates* by boiling *mesotartaric acid* with methyl alcohol and resolving the resulting racemic ester with strychnine.

TARTRAZINE *v.* PYRAZOLONE COLOURING MATTERS.

TARTRONIC ACID, *hydroxymalonic acid* $\text{HO}\cdot\text{CH}(\text{CO}_2\text{H})_2$, discovered by Dessaignes in 1853 as a decomposition product of an aqueous solution of dinitrotartaric acid and hence named *tartronic acid* (Annalen, 1852, 82, 363; 1854, 89, 339; compare Demole, Ber. 1877, 10, 1788); is also obtained by reducing mesoxalic acid with sodium amalgam (Deichsel, Zeitsch. Chem. 1865, 69); by the action of baryta water or of silver oxide on monobromomalonic acid (Pinner, Ber. 1875, 8, 963; Petrieff, *ibid.* 1878, 11, 414); by hydrolysing ethyl monochloromalonate with potassium hydroxide and decomposing the calcium salt with oxalic acid (Conrad and Bischoff, *ibid.* 1880, 13, 595); by the action of baryta water on dibromopyruvic acid (Grimaux, Bull. Soc. chim. 1877, [ii.] 27, 440); or of dilute sodium hydroxide on ethyl trichlorolactate (Pinner, 1885, Ber. 18, 752). Tartronic acid can be obtained by the careful oxidation of glycerol with nitric acid (Sadler, *ibid.* 1875, 8, 1456) or potassium permanganate (Campani and Bizzarri, Gazz. chim. ital. 1880, 10, 489; compare *ibid.* 1883, 13, 490); or by the action of fuming nitric acid and phosphoric oxide on tartaric acid (Behrend and Osten, Annalen, 1905, 343, 152; Fisher and Simons, J. Amer. Chem. Soc. 1921, 43, 628); and it has been synthesised by treating glyoxylic acid with potassium cyanide and boiling the product with baryta water (Böttinger, Ber. 1881, 14, 729); *v.* Lippmann (Ber. 1913, 46, 3862) for the isolation of tartronic acid from a sugar syrup. Tartronic acid is most conveniently prepared by heating an aqueous solution of dihydroxytartaric acid until carbon dioxide ceases to be evolved and finally evaporating the solution (Fenton, Chem. Soc. Trans. 1898, 73, 73; compare Gruber, Ber. 1879, 12, 514).

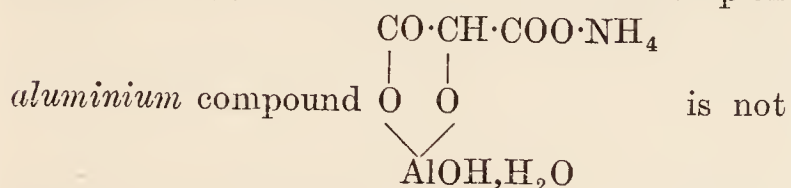
Tartronic acid crystallises from water in large, hard, anhydrous prisms; it sublimes when carefully heated at 110° – 120° (Conrad and Bischoff, *l.c.*); melts at 158° – 159° (Fenton, *l.c.*; Skinner, Chem. Soc. Trans. 1898, 73, 489); at 155° (Gruber, *l.c.*; Massol, Compt. rend. 1892, 114, 422); at 145° – 160° (Grimaux, *l.c.*); melts and decomposes at 185° – 187° (Conrad and Bischoff, *l.c.*); at 178° – 180° (Campani and Bizzarri, Gazz. chim. ital. 1882, 12, 1); at 184° (Pinner, *l.c.*); at 183° (Böttinger, *l.c.*). The correct value appears to be 156° – 158° (decomp.) (Behrend and Prüsse, Ann. 1918, 416, 233). It has electrical conductivity $\mu_D = 357$ (Ostwald, Zeitsch. Physikal. Chem. 3, 369), affinity constant $K = 0.107$ (Skinner, *l.c.*); for heats of neutralisation compare Gal and Werner (Compt. rend. 1886, 103, 871, and Massol (*l.c.*). It is readily oxidised by hydrogen peroxide in the presence of ferrous salts into mesoxalic acid (Fenton, Chem. Soc. Trans. 1900, 77, 71).

Salts.—Tartronic acid forms both normal and acid salts, which, with the exception of the salts of the alkali metals, are insoluble or only sparingly soluble in water (Pinner, Ber. 1885, 18, 752). The following salts are described:—*Ammonium* $\text{C}_3\text{H}_2\text{O}_5(\text{NH}_4)_2$ and $\text{C}_3\text{H}_3\text{O}_5(\text{NH}_4)$

(Dessaigues, *l.c.*); sodium $C_3H_2O_5Na_2$ is deliquescent and becomes anhydrous at 110° , the acid salt is unstable; potassium $C_3H_2O_5K_2$ and $C_3H_3O_5K \cdot \frac{1}{2}H_2O$ (Conrad and Bischoff, *l.c.*; Massol, *l.c.*); barium $C_3H_2O_5Ba \cdot 2H_2O$; calcium $C_3H_2O_5Ca \cdot 2\frac{1}{2}H_2O$ (Pinner, *l.c.*); zinc and mercury salts are white precipitates, cobalt salt is a red flocculent precipitate; the copper salt bluish-green crystals (Conrad and Bischoff, *l.c.*); lead salts $C_3H_2O_5Pb$ and $(C_3HO_5)_2Pb_3 \cdot 2H_2O$; cadmium salt $C_3H_2O_5Cd$ (Gruber, *l.c.*); silver salt $C_3H_2O_5Ag_2$ is crystalline (Conrad and Bischoff, *l.c.*); manganese salt



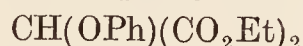
crystallises in the triclinic system (Campani and Bizzarri, *l.c.*); the aluminium in the complex



precipitated by ammonia (Hanuš and Quadrat, Zeitsch. anorg. Chem. 1909, 63, 306).

Derivatives.—The methyl ester $HO \cdot CH(CO_2Me)_2$ has m.p. 44.5° – 45° (Filippo, *l.c.*), 53.3° – 53.5° (corr.) (Fisher and Simons, J. Amer. Chem. Soc. 1921, 43, 628); b.p. $122^\circ/19$ mm. (Filippo, *l.c.*); the chloro derivative $HO \cdot CCl(CO_2Me)_2$ has m.p. 42° , is unstable and converted into methyl dihydroxymalonate on exposure to moist air; the bromo derivative $HO \cdot CBr(CO_2Me)_2$, m.p. 30° (decomp.) dissociates at 40° into hydrogen bromide and methyl mesoxalate; the anilino derivative $PhNH \cdot C(OH)(CO_2Me)_2$ has m.p. 102° and yields methyl phenyliminomalonate $NPh : C(CO_2Me)_2$ by the action of phosphoric oxide (Curtiss and Spencer, J. Amer. Chem. Soc. 1909, 31, 1053).

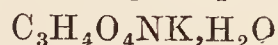
The ethyl ester $HO \cdot CH(COOEt)_2$ has m.p. 2° , b.p. 120.5° – $121^\circ/15$ mm. (Filippo, Rec. trav. chim. 1910, [ii.] 14, 113; Freund, Ber. 1884, 17, 780; Pinner, *l.c.*); it forms an acetate $CH(OAc)(CO_2Et)_2$, b.p. 235° – 245° under atmospheric pressure, or 158° – $163^\circ/60$ mm., of which the ethyl derivative $CEt(OAc)(CO_2Et)_2$ has b.p. 151° – $153^\circ/30$ mm. (Conrad and Brückner, Ber. 1891, 24, 2997); the phenyl ether



has b.p. 230° – $240^\circ/60$ mm., and yields the crystalline acid $CH(OPh)(COOH)_2$ on hydrolysis.

Ethyl cyanotartronate, $OH \cdot C(CN)(CO_2Et)_2$, is an undistillable oily liquid, $D_{30}^{20} 1.16$, Curtiss and Nickell (J. Amer. Chem. Soc. 1913, 35, 885)

Tartronamic acid $CO_2H \cdot CH(OH)CONH_2$ prepared by boiling freshly prepared sodium dialurate with water, forms large needles or prismatic crystals, m.p. 160° (decomp.), and yields crystalline barium $(C_3H_4O_4N)_2Ba \cdot H_2O$, lead $(C_3H_4O_4N)_2Pb \cdot \frac{1}{2}H_2O$; potassium



and silver $C_3H_4O_4NAg$ salts (Menschutkin, Annalen, 1876, 182, 82).

Tartronamide $HO \cdot CH(CONH_2)_2$ has m.p. 195° – 196° (Pinner, *l.c.*), 198° (Freund, *l.c.*) and gives the biuret reaction (Schiff, Ber. 1896, 29, 298, 1354). **Tartrondimethylamide**

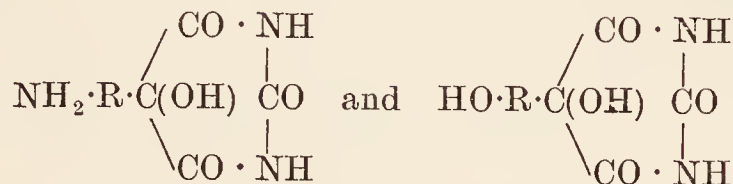


has m.p. 153° – 154° (Filippo, *l.c.*).

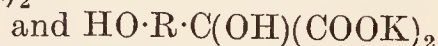
The p-nitrophenylosazone of tartronic semi-aldehyde forms rosettes of fine needles, m.p. 310° (corr.) (Dakin, Bio-Chem. J. 1919, 13, 398).

Alkyl substituted tartronic acids.—Methyl tartronic acid $HO \cdot CMe(CO_2H)_2$ has m.p. 178° (Schmöger, J. pr. Chem. [ii.] 14, 77; 19, 168; 24, 38; Böttlinger, Ber. 1881, 14, 87, 148; 1884, 17, 114); ethyltartronic acid $HO \cdot CEt(CO_2H)_2$ has m.p. 98° (Guthzeit, Annalen, 1881, 209, 232); isobutyltartronic acid $HO \cdot C(C_4H_9)(CO_2H)_2$ has m.p. 110° – 114° (Conrad and Bischoff, Annalen, 1881, 209, 218; cf. Plattner (Monatsh. 1915, 36, 899); benzyltartronic acid $CH_2Ph \cdot C(OH)(CO_2H)_2$ has m.p. 143° ; all these acids decompose at their melting-point, yielding the corresponding member of the acetic acid series.

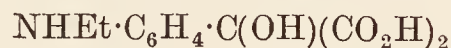
Aryl substituted tartronic acids.—Alloxan condenses with aromatic amines, phenols or polyhydric phenols in the presence of condensing agents to form compounds of the types



and these are readily hydrolysed by alkali to give the alkali salt of the corresponding substituted tartronic acid



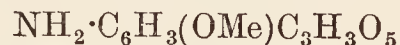
from which the acid is usually easily derived. The following acids obtained by these methods are described in the patent literature (D. R. PP. 107720, 112174, 113722, 114904, 115817):—**p-ethylaminophenyltartronic acid**



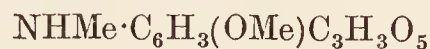
m.p. 163° (decomp.); **p-diethylaminophenyltartronic acid** $NEt_2 \cdot C_6H_4 \cdot C_3H_3O_5$, m.p. 107° – 108° (decomp.); **p-benzylaminophenyltartronic acid** $C_7H_7NH \cdot C_6H_4 \cdot C_3H_3O_5$, m.p. 137° (decomp.); **potassium hydrogen p-ethylbenzylaminotartronate** $C_7H_7NEt \cdot C_6H_4 \cdot C_3H_2O_5K$; **p-phenylaminophenyltartronic acid** $NHPh \cdot C_6H_4 \cdot C_3H_3O_5$, m.p. 125° – 127° (decomp.); **p-iminodiphenyltartronic acid** $NH(C_6H_4 \cdot C_3H_3O_5)_2$ as potassium hydrogen salt only; **p-amino-m-tolyltartronic acid**



m.p. 194° – 195° (decomp.); **p-ethylamino-m-tolyltartronic acid** $NHEt \cdot C_7H_6 \cdot C_3H_3O_5$; **p-amino-m-methoxyphenyltartronic acid**



m.p. 187° – 188° (decomp.); **p-methylamino-m-methoxyphenyltartronic acid**



m.p. 135° (decomp.); **p-amino-m-ethoxyphenyltartronic acid**, m.p. 150° (decomp.); **p-amino-o-chlorophenyltartronic acid** $NH_2 \cdot C_6H_3Cl \cdot C_3H_3O_5$, m.p. 198° – 199° (decomp.); **p-dimethyl- and p-diethyl-amino-o-chlorophenyltartronic acids** as potassium hydrogen salts only; **p-ethylenediaminodiphenyltartronic acid** $C_2H_4N_2H_2(C_6H_4 \cdot C_3H_3O_5)_2$ decomposes at 400° ; **o-hydroxyphenyltartronic acid** $HO \cdot C_6H_4 \cdot C_3H_3O_5$, m.p. 118° – 120° (decomp.); **p-hydroxy-m-methoxy-phenyltartronic acid**; **o-hydroxy-m-tolyltartronic acid**; and **m-p-dihydroxyphenyltartronic acid**. M. A. W.

TASAJO is a preserved meat exported from Rio de la Plata, and consists of salted and pressed flesh which has been sun-dried. A similar unsalted preparation consumed by the natives, but unsuitable for export, is known as 'charque.' The following analyses of *tasajo* are given:

	Per cent.	Per cent.
Water . . .	20.98	20.90
Albuminoids . .	23.25	20.48
Fat . . .	45.15	45.06
Ash . . .	13.51	—
(Including salt)	11.63	—

Biological experiments proved that '*tasajo*' is rich in vitamins A and B (A. Bickel and J. A. Collazo, *Zeitsch. Nahr. Genussm.* 1923, 46, 360; *Analyst*, 1924, 49, 187).

TASMANITE v. RESINS.

TASTE. Considering the facts that (1) optical isomerides have different taste, (2) substitutions always affect the taste, (3) all the compounds containing either Cohn's sapophore group or Oertly and Meyer's glucophore contain vibratory hydrogen, and (4) the taste of electrolytes is due to the sum of the tastes of molecular electrolyte, anions, cations, and complex ions Kodama (*J. Tokyo Chem. Soc.* 1920, 41, 495) proposes a theory that the taste of organic substances is due to electric vibration of the sapophoric element (*Chem. Soc. Abstr.* 1920, i. 786).

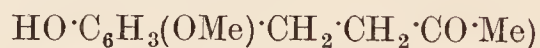
The taste system is composed of the sensory particles and their components and the liquid or solution; it is thus a heterogeneous system, one part of which comprises the colloidal protoplasmic taste cells or nerve terminations, and the other liquid or solutions. The main changes which occur depend on alteration of surface and electrical energy. Equally marked sensations of taste must correspond with the adsorption of equal amounts of the substance by the organs of taste. The concentration necessary to induce taste with the alkali salts is an additive function of the inverse values of the rates of migration of the ions. The concentration for barium and calcium chlorides is less than that for the alkali salts, whilst for aluminium chloride a minimum value is attained. Valency is therefore an important factor, and this appears to indicate a suspensoid character of the adsorption in the system of taste. In addition to the rate of adsorption, electrical phenomena are also important in their effect on the induction of taste by different electrolytes. The phenomena of the sensation of taste produced by homologous and isomeric compounds are explicable on the assumption that the process is one of adsorption. Experimental investigation confirms the accuracy of a deduction, from which it appears that the sensation of taste is more persistent with increasing concentration of tasted substances and increasing adsorption exponent, and with decreasing inducing concentration and rate of diffusion. Renqvist (*Chem. Zentr.* 1920, ii. 591) also examines the qualities of taste, their variation with differing concentrations of electrolyte, and their relationships to the differences of potential caused by the electrolyte in the sensory system. The quality of the induced taste can be foretold with some degree of accuracy if the rate of

migration of the ions of a univalent electrolyte and its concentration are known. The 'compensation of taste' is a peripheral phenomenon which is observed in the sensory system; a bitter taste is not, however, compensated. The 'fundamental tastes'—sweet, bitter, and sour—are chosen, from which, in analogy to the Young-Helmholtz theory of colour vision, all the various sensations of taste can be compounded (*Renqvist, Chem. Soc. Abstr.* 1920, i. 786).

According to Renqvist (*Chem. Zentr.* 1920, iii. 425) the concentrations requisite to produce the sensation of taste have been estimated for six different alkyl esters of cyanoacetic acid, the methyl and ethyl esters of oxalic, malonic, and succinic acids, the homologous monohydroxy-alcohols from methyl to octyl alcohol, and various isomeric esters of certain ether acids. In the majority of cases, the results are in agreement with the relationships established previously between the inducing concentration for taste and the coefficients of diffusion. The inducing concentrations of isomerides are approximately equal, whilst with homologous compounds they diminish with increasing molecular weight. The surface tensions of isomeric substances at the inducing concentration are determined by the drop method, and found to be approximately equal (*Renqvist, Chem. Soc. Abstr.* 1920, i. 787).

All the normal alkyl-chloromalonamides have a decidedly sweet taste, the *n*-butyl derivative being both bitter and sweet. Dichloromalonamide, and ethyl-, *n*-propyl-*iso*-propyl-, and *n*-butylchloromalonamides have about nine times the sweetening power of sucrose. The maximum sweetness was observed with the *n*-hexyl derivative, of which 1 part in 5000 of water had the sweetness of a 5 p.c. solution of sucrose. This observation was confirmed by comparison with a solution of 'dulcin' (*p*-phenetyl-urea), which is stated to be 250 times as sweet as sucrose. On the other hand, the *iso*-butyl, *iso*-amyl, and benzyl derivatives stand in sharp contrast to the other members of the series, being decidedly bitter and without any sweet taste. No constant variation in sweetness could be established in the series. The sweet taste of the hexyl derivative is free from any disagreeable after-taste, but the compound has the drawback of being difficult to dissolve in water (A. W. Dox and B. Houston, *J. Amer. Chem. Soc.* 1924, 46, 1278; *Analyst*, 1924, 49, 345).

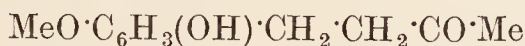
Vanillin and piperonal possess pleasant odours, whereas zingerone (methyl 4-hydroxy-3-methoxyphenylethyl ketone



and the analogous 3:4-methylenedioxyphenylethyl methyl ketone have a pungent taste, but the intermediate products in the synthesis of these substances from vanillin and piperonal, namely, 4-hydroxy-3-methoxystyryl methyl ketone $\text{HO}\cdot\text{C}_6\text{H}_3(\text{OMe})\cdot\text{CH}:\text{CH}\cdot\text{CO}\cdot\text{Me}$ and 3:4-methylenedioxy-styryl methyl ketone, are almost tasteless when first brought into contact with the tongue, although they gradually develop pungency. A number of compounds of similar constitution have been examined with a view to discover the influence of constitutional

variations on the taste. As in the above case of 4-hydroxy-3-methoxystyryl methyl ketone, the primary condensation product is generally less readily soluble than its final reduction product in organic solvents, and does not immediately taste pungent, whereas the reduction products are markedly pungent; styryl methyl ketone is exceptional in being readily soluble and having a very tingling taste. The presence of a free phenolic group is not essential to pungency, because phenylethyl methyl ketone, *p*-methoxyphenylethyl methyl ketone, and 3:4-methylenedioxyphenylethyl methyl ketone are all pungent. The degree of pungency, however, is greatly influenced by the position of the free hydroxyl group with respect to the ketonic side-chain; *o*-hydroxyphenylethyl methyl ketone in taste resembles 2-hydroxy-3-methoxyphenylethyl methyl ketone, and *p*-hydroxyphenylethyl methyl ketone resembles zingerone. As in these cases the hydroxyphenylethyl methyl ketones are less pungent than the corresponding hydroxymethoxyphenylethyl methyl ketones, the *m*-methoxyl group appears to increase the pungency. The influence of the simple hydrocarbon radicle attached to the ketonic group is not much greater than that of the position of the hydroxyl group, because phenyl 4-hydroxy-3-methoxyphenylethyl ketone has a pungent taste similar to zingerone.

The pungent taste of 2-hydroxy-3-methoxyphenylethyl methyl ketone



is accompanied by a paralysing effect, which is also observed with *o*-hydroxyphenylethyl methyl ketone (Nomura and Nozawa, Chem. Soc. Abstr. 1918, i. 438).

According to Oertly and Myers the taste of sweet substances depends on two factors, the presence of a glucophore and an auxogluc. An auxogluc is an atom or radicle which, combined with any glucophore, yields a sweet compound. A glucophore is a group of atoms which has the power to form sweet compounds by uniting with a number of otherwise tasteless atoms or radicles. This theory is considered in the paper only in connection with aliphatic compounds. In the sense of the theory the following radicles are glucophores:

- (1) $-\text{CO} \cdot \text{CH}(\text{OH})-(+\text{H})$;
- (2) $\text{CO}_2\text{H} \cdot \text{CH}(\text{NH}_2)-$;
- (3) $-\text{CH}_2 \cdot \text{O} \cdot \text{NO}_2$;
- (4) $\text{CH}_2(\text{OH}) \cdot \text{CH}(\text{OH})-$;
- (5) $\text{C}_{\frac{\text{H}_2-x}{\text{Hal}^x}}$;
- (6) $\text{C}_{\frac{\text{H}_3-x}{\text{Hal}^x}} \cdot \text{C}_{\frac{\text{H}_2-y}{\text{Hal}^y}}$.

The following atoms or radicles act as auxogluces, forming sweetish compounds with glucophores: (a) hydrogen, (b) the radicles $\text{C}_n\text{H}_{2n+1}$, containing 1-3 carbon atoms, (c) the radicles $\text{C}_n\text{H}_{2n+1} \cdot \text{O}-$ of the monohydric alcohols where $n=1$ or 2, (d) the radicals $\text{C}_n\text{H}_{2n-1}\text{O}_n$ of the polyhydric alcohols. A very long list of sweet substances supporting this theory is given. The presence of the phenyl group tends to make an otherwise sweet compound bitter. Some exceptions to the rule are found in stereoisomeric substances; thus *l*-valine $\text{CHMe}_2 \cdot \text{CH}(\text{NH}_2) \cdot \text{CO}_2\text{H}$ is made up of glucophore

$-\text{CH}(\text{NH}_2) \cdot \text{CO}_2\text{H}$, and the auxogluc, CHMe_2- , and is slightly bitter, but *d*-valine and *dl*-valine are both sweet (Oertly and Myers, J. Amer. Chem. Soc. 1919, 41, 855; Chem. Soc. Abstr. 1919, i. 422).

The elucidation of the constitution of capsaicin by Nelson (Chem. Soc. Abstr. 1919, i. 543) is made the basis of an examination of the extent to which the various features of the molecule contribute to produce the peppery taste characteristic of that substance.

Capsaicin is the vanillylamide of a decenoic acid



and it is known that the vanillylamide of Δ^{ω} -undecenoic acid has a similar and about equally sharp taste. When undecenoic acid is condensed with a number of bases more or less closely related to vanillylamine, it is found that the *p*-hydroxybenzylamide (m.p. 86°) has a taste considerably weaker than that of capsaicin, whilst the taste of the *o*-hydroxybenzylamide (not purified) is weaker still. Hence the presence of the methoxy group and the particular orientation of the hydroxyl group in capsaicin both contribute to its taste. The presence of a phenolic hydroxyl group appears to be essential, since both the *anisylamide* (white leaflets, m.p. 91°) and the *benzylamide* (m.p. 51° - 52°) are tasteless. So also is the *p*-hydroxyphenylamide (m.p. 107°), which shows that the component amine must be of aliphatic type.

With regard to the conditions governing the character of the acid residue, it is found that the vanillylamides of Δ^{α} -nonenoic acid, decenoic acid, and Δ^{ω} -undecenoic acid, have tastes of a comparable strength, whilst those of Δ^{β} -hexenoic acid and crotonic acid possess much less pungent tastes. The taste of the vanillylamide of cinnamic acid (white powder, m.p. 138°) was also only feebly peppery, whilst that of the vanillylamide of oleic acid was exceedingly pungent but of different quality from the tastes of capsaicin and its closer homologues.

On the other hand, the *p*-hydroxybenzylamide of Δ^{α} -nonenoic acid tastes more strongly peppery than the corresponding amide of undecenoic acid. These facts show (a) that the positions of the double bond in the acid residue has comparatively little influence on the peppery taste of the capsaicin-like amides, (b) that, on the other hand, the length of the carbon chain is important, acids with nine, ten, or eleven carbon atoms showing the phenomenon in the most marked and characteristic manner.

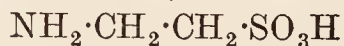
One of the most remarkable facts which emerged from the investigation is the necessity for an unsaturated linking in the acid component.

The vanillylamide (m.p. 86°) of highly purified stearic acid is quite without taste, both in the solid state and in concentrated alcoholic solution. Commercially 'pure' palmitic acid, on the other hand, gives a vanillylamide (m.p. 79°) which has a sharp taste, but this is due to the presence of traces of the oleic acid derivative. When the amide is purified by crystallisation from ether, the taste of the solid amide vanishes, but it is still intense in alcoholic solution. A very delicate test for unsaturated acid may be based on these results.

The piperidide of sorbic acid (m.p. 77°) has

a taste which is very bitter but not at all peppery (Ott and Zimmermann, *Annalen*, 1921, 425, 314; *Chem. Soc. Abstr.* 1922, i. 137).

TAURINE, α -amino- β -ethane sulphonic acid

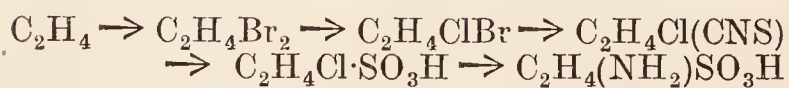


in combination with cholic acid forms one of the chief constituents of the bile of oxen and other animals, whence it was obtained by Gmelin in 1826; it was afterwards investigated by Demarcay (*Annalen*, 1838, 27, 286) and by Dumas and Pelouze (*ibid.* 292,) who overlooked the fact that it contained sulphur and gave it the formula $\text{C}_2\text{H}_7\text{NO}_5$. Redtenbacher (*ibid.* 1846, 57, 170), remarking on the strangely inert behaviour towards strong acids of a compound containing so large a proportion of oxygen, reinvestigated the compound, and on fusion with alkali obtained evidence of the presence of sulphur, and gave it the correct formula $\text{C}_2\text{H}_7\text{NO}_3\text{S}$. *Taurodeoxycholic acid*



prepared from deoxycholic acid azide, forms colourless, hygroscopic, prismatic needles, which have an indefinite m.p. 175° – 200° (Wieland, *Zeitsch. physiol. Chem.* 1919, 106, 181). Taurine occurs in the muscles and organs of Bojanus of *Mytilus edulis* (Kelly, *Beitr. chem. Physiol. Path.* 1904, 5, 377); in the extract of muscle and the hepato-pancreas of various marine gasteropods (Mendel, *ibid.* 582); and in meat extract (Micko, *Zeitsch. Nahr. Genussm.* 1908, 15, 449; *Zeitsch. physiol. Chem.* 1908, 56, 180), in the flesh of the herring (*Clupea harengus*) (Berner, *Zeitsch. physiol. Chem.* 1920, 110, 172). Taurine can be prepared in large quantities from the muscle of the abalone, *Haliotis*, 74 kilograms yielding 362 grams of taurine (Schmidt and Watson, *J. Biol. Chem.* 1918, 33, 499). The source of the taurine in the animal economy is the cystine of the ingested protein, the oxidation occurring in the liver; experiments on dogs serve to show that the administration of cystine leads to an increase in the output of taurine (Von Bergmann, *Beitr. chem. Physiol. Path.* 1903, 4, 192); and experiments on cats show that if artificial cystinuria is produced there is a consequent fall in the taurine of the bile (Gibson, *Proc. Amer. Soc. Biol. Chem.* 1908, 16).

Synthesis. Taurine can be synthesised from ethylene by the following series of reactions:—ethylene dibromide is converted by the action of antimony pentachloride into ethylene chlorobromide, which on treatment with potassium thiocyanate yields ethylene chlorothiocyanate; this is converted by oxidation into chloroethanol sulphonic acid, the silver salt of which reacts with ammonia at 100° – 120° , yielding taurine



(James, *Chem. Soc. Trans.* 1879, 35, 810; compare Kolbe, *Annalen*, 1862, 122, 33). Taurine can also be readily prepared from cysteic acid (α -amino- β -sulphopropionic acid) by heating it with water in a sealed tube at 235° – 240°

$\text{SO}_3\text{H} \cdot \text{CH}_2 \cdot \text{CH}(\text{NH}_2)\text{CO}_2\text{H} \rightarrow \text{SO}_3\text{H} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NH}_2$
(Friedmann, *Beitr. Chem. Physiol. Path.* 1903, 3, 1). It may be prepared on an industrial scale from acetaldehyde and chlorosulphonic acid,

(Auzies, *Rev. gen. chim. pure appl.* 1911, 14, 278); and a yield of 70 p.c. is afforded by the action of ammonium sulphite solution on bromoethylamine hydrochloride (Reychler, *Bull. Soc. chim. Belg.* 1923, 32, 247).

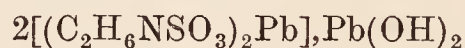
Taurine crystallises in large tetragonal plates or well-developed crystals belonging to the prismatic class of the monoclinic system $a : b : c = 0.6817 : 1 : 0.9073$, $\beta = 93^\circ 47'$, that decompose on heating above 240° ; it is soluble in 15.5 parts of water at 12° , or in 25,000 parts of 90 p.c. alcohol at 17° (Stutzer, *Zeitsch. anal. Chem.* 1892, 31, 503). For specific electric conductivity, see Reychler, *l. c.*

When taurine is administered to human subjects or to dogs, it is eliminated partly unchanged and partly in the form of taurocarbamic acid (*v. infra*; Salkowski, *Ber.* 1873, 6, 744). Schmidt and Allen (*J. Biol. Chem.* 1920, 42, 55), however, were unable to confirm this statement. The administration of 3 to 10 grms. to man is followed by an increased elimination of neutral sulphur in the urine; from 59 to 86 p.c. of the taurine sulphur is thus recoverable from the urine. Large doses of taurine administered to rabbits or to human subjects produce no toxic effects (Schmidt, von Adelung and Watson, *J. Biol. Chem.* 1918, 33, 501); when fed to fowls a considerable portion reappears unchanged in the excreta (Čech, *ibid.* 1877, 10, 1461); and it can replace cystine in the diet of mice (Mitchell, *Austral. J. Exp. Biol.* 1924, 1, 5).

For the detection of taurine in urine, *v. Bergell* (*Zeitsch. physiol. Chem.* 1916, 97, 260), and for its estimation in muscle, *v. Okuda and Sanada* (*J. Coll. Agr. Imp. Univ. Tokyo*, 1919, 7, 77).

Taurine possesses considerable germicidal power, Bertarelli (*Centr. Bakt. Parasitenk.* 1, Abt. 67, 100f rom *Amer. Chem. Abs.* 1913, 625; *v. also*, Takeoka, *Amer. Chem. Abs.* 1917, 1990; from *J. Infect. Dis.* 1917, 20, 442).

Salts. Taurine has a neutral reaction, and forms salts with bases, the *silver* $\text{C}_2\text{H}_6\text{NSO}_3\text{Ag}$; *lead* $(\text{C}_2\text{H}_6\text{NSO}_3)_2\text{Pb}$ and



sodium $\text{C}_2\text{H}_6\text{NSO}_3\text{Na}$ and *calcium* $(\text{C}_2\text{H}_6\text{NSO}_3)_2\text{Ca}$ salts are crystalline and soluble; the *cadmium* salt $(\text{C}_2\text{H}_6\text{NSO}_3)_2\text{Cd}$ is a sparingly soluble white powder, and *mercury* salt $(\text{C}_2\text{H}_6\text{NSO}_3)_2\text{Hg}$ is insoluble in cold and sparingly soluble in hot water and is well adapted for the preparation of pure taurine and for its detection (Lang, *Ber.* 1876, 9, 853; *Bull. Soc. chim.* 1876, [ii.] 25, 180).

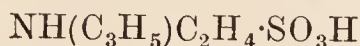
Derivatives. *Ethanesulphonimide* or *anhydrotaurine* C_2H_4 $\begin{matrix} \text{NH} \\ | \\ \text{SO}_2 \end{matrix}$ obtained by the action of

ammonia on β -chloroethane sulphonic chloride is a gum-like solid, m.p. 45° – 50° ; is not decomposed on heating with water at 150° , and yields a mercury derivative $(\text{C}_2\text{H}_4\text{O}_2\text{NS})_2\text{Hg}$ with mercuric oxide (James, *Chem. Soc. Trans.* 1886, 49, 486).

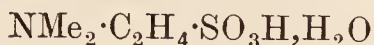
The following mono-, di- and tri-substituted taurines are obtained by heating the amine salt of β -chloroethane sulphonic acid with the necessary quantity of the amine at 160° in a sealed tube for 10 hours:—

Methyltaurine $\text{NHMe} \cdot \text{C}_2\text{H}_4 \cdot \text{SO}_3\text{H}$, m.p. 241° – 242° , forms lustrous prisms belonging to the

anorthic system; *ethyltaurine* $\text{NHEt} \cdot \text{C}_2\text{H}_4 \cdot \text{SO}_3\text{H}$
rhombic prisms, m.p. 147° ; *allyltaurine*



rhombic prisms, m.p. 190° – 195° ; *phenyltaurine*
 $\text{NHPh} \cdot \text{C}_2\text{H}_4 \cdot \text{SO}_3\text{H}$, thin silky leaves, m.p. 277° – 280° (decomp.). *Dimethyltaurine*



darkens at 270° – 280° and finally decomposes;
diethyltaurine $\text{NEt}_2 \cdot \text{C}_2\text{H}_4 \cdot \text{SO}_3\text{H}$, m.p. 151° ;
methylphenyltaurine $\text{NMePh} \cdot \text{C}_2\text{H}_4 \cdot \text{SO}_3\text{H}$. *Tri-*
methyltaurine is an analogue of betaine and
probably has the constitution represented by
the formula $\text{C}_2\text{H}_4 \langle \text{NMe}_3 \rangle \text{O}$, since it yields
pure trimethylamine when boiled with excess of
baryta, and does not give any trace of methyl
iodide on heating with hydrogen iodide; it
crystallises in rhombic plates that remain un-
changed at 300° (James, Chem. Soc. Trans.
1885, 47, 367; 1886, 49, 486; Dittrich, J. pr.
Chem. 1878, [ii.] 18, 63). *Taurocyamine*

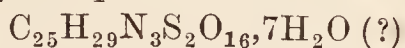


obtained by heating taurine and cyanamide at
 100° – 120° forms soluble white prisms, m.p. 224° – 226° ; *methyltaurocyamine*



similarly formed from methyltaurine crystallises
in large monoclinic prisms that become anhy-
drous at 110° and turn brown at 285° (Dittrich,
l.c.). *Phenyltaurocyamine* forms glistening leaves
that do not melt at 300° ; *dimethyltaurocyamine*
 $(\text{CH}_3)_2(\text{CN} \cdot \text{NH}_2)\text{C}_2\text{H}_4 \cdot \text{SO}_3\text{H}$ has m.p. 248° (de-
comp.) (James, Chem. Soc. Trans. 1885, 47,
367).

Taurine condenses with benzoic and with
phthalic anhydride to form the compounds
 $\text{C}_{15}\text{H}_{20}\text{N}_2\text{S}_2\text{O}$, m.p. 175° , and



m.p. 50° , respectively (Tauber, Beitr. chem.
Physiol. Path. 1903, 4, 323).

Taurine reacts with α -naphthylcarbimide to
form the corresponding hydantoic acid (Schmidt,
Proc. Soc. Exp. Biol. Med. 1921, 18, 204).

Taurocarbamic acid, α -carbamido- β -ethane
sulphonic acid, $\text{NH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{SO}_3\text{H}$,
occurs in the urine after the administration of
taurine, and probably also in normal urine.
The potassium salt is readily prepared from
taurine and potassium cyanate (Salkowski, Ber.
1873, 6, 1191). The acid is also prepared by
oxidising ethylenepseudothiourea with bromine
water (Gabriel, *ibid.* 1889, 22, 1142); or by
condensing taurine with urea in the presence of
barium hydroxide (Lippich, *ibid.* 1908, 41,
2968).

Taurocarbamic acid forms prismatic crystals
that begin to decompose in a closed tube at 160° ,
the mass again becomes crystalline and melts
at 300° with decomposition. M. A. W.

TAUROCHOLIC ACID $\text{C}_{26}\text{H}_{45}\text{NO}_7\text{S}$ occurs
in the form of its sodium salt as one of the chief
constituents of the bile salts. It yields taurine
and cholic acid on hydrolysis; and has been
synthesised by condensing the azide of cholic
acid $\text{C}_{23}\text{H}_{39}\text{O}_3 \cdot \text{CON}_3$ with an alkaline solution
of taurine (Bondi and Müller, Zeitsch. physiol.
Chem. 1906, 47, 499; compare, Tauber, Beitr.
chem. Physiol. Path. 1903, 4, 323), *v. BILE and*
CHOLIC ACID.

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Taurodeoxycholic acid



was prepared from deoxycholic acid azide in
the form of colourless, hygroscopic, prismatic
needles grouped in rosettes, m.p. 175° – 200° , not
sharp.

Attempts to prepare glycocholic acid and
taurocholic acids by combining the conjugated
deoxycholic acids with stearic acid failed
(Wiand and Stender, Zeitsch. physiol. Chem.
1919, 106, 181; Chem. Soc. Abstr. 1919, i.
576).

TAXINE $\text{C}_{37}\text{H}_{51}\text{NO}_{10} (?)$ is an alkaloid
which is supposed to form the poisonous con-
stituent of the leaves, shoots, and fruit of the
yew tree (*Taxus baccata* (Linn.)). It was dis-
covered by Lucas (J. 1856, 550; Arch. Pharm.
1857, 85, 145), but was first prepared more or
less pure by Marmé in 1876 (Hilger and Brande,
Ber. 1890, 23, 464). It may be obtained
by extracting the powdered leaves and seeds
with ether or hot alcohol, and after distilling
off most of the solvent, treating the residue with
dilute acid and then precipitating with ammonia,
the last two processes being repeated until the
product becomes colourless. A better yield
is said to be obtained by extracting the leaves,
&c., with water acidified with sulphuric, tartaric,
or oxalic acid (Vreven, Pharm. J. 1896, 4,
215; Sauvan, *ibid.* 177; Thorpe and Stubbs,
Chem. Soc. Trans. 1902, 874; Moss, Sci. Proc.
Roy. Dublin Soc. 1909, 12, 92. See also Amato
and Capparelli, Gazz. chim. ital. 10, 349;
Marmé, Chem. Zentr. 1876, 166).

From two specimens of the leaves of a female
Irish yew, Moss obtained 0.323 p.c. and 0.623
p.c., from the seeds of the fruit of the same, 0.079
and 0.082 p.c.; whilst from the leaves of a male
specimen he obtained 0.082 p.c. The fleshy
part of the berries, however, contained no
taxine. From the common yew, both male and
female, Thorpe and Stubbs obtained about
0.18 p.c. taxine.

According to Winterstein and Iatrides
(Zeitsch. physiol. Chem. 1921, 117, 240) taxine
forms 0.7–1.4 p.c. of the dry matter of the
needles of yew, and has the formula $\text{C}_{37}\text{H}_{51}\text{O}_{10}\text{N}$.

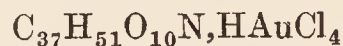
Taxine is a dull, white, amorphous powder.
Neither the alkaloid nor its salts can be obtained
crystalline. The amorphous base sinters at
 97° and melts at 105° – 110° $[\alpha]_D + 53.15^\circ$ in
1 p.c. sulphuric acid, $+ 51.52^\circ$ in absolute
alcohol. By microscopic examination, Moss
detected signs of softening at 60° . It is odour-
less, has a very bitter taste, is almost insoluble
in water, and in light petroleum, but is readily
soluble in ether, alcohol, acetone, chloroform,
or benzene, also in dilute acids and to a slight
extent in excess of ammonia. When heated
in a glass tube, a white cloud appears and drops
of oil condense and then solidify on the cool
parts of the tube. When treated with hydro-
chloric acid, it decomposes readily (Thorpe and
Stubbs, *l.c.*; Moss, *l.c.*). With sulphuric acid
it gives a brown to purplish-blue colour; whilst
if nitric acid is present the colour is a very deep
pink. With reagents generally it gives the
characteristic alkaloid reactions. When heated
with soda lime, ammonia is evolved. On
hydrolysis with acids a resinous substance,
cinnamic acid and acetic acid are obtained.

It takes up 2 mols. of hydrogen, four acetyl groups, and 2 mols. of bromine. A methiodide can also be prepared. With potassium permanganate, benzoic acid, acetic acid, benzonitrile and a reducing substance are obtained (Winterstein and Iatrides, *l.c.*). Taxine forms a series of soluble salts with acids and characteristic double salts with a number of metallic salts.

Taxine depresses the action of the heart in frogs, rabbits, cats and dogs. It interferes with the respiration and causes death in a short time through suffocation.

Heisaburo Kondo (J. Pharm. Soc. Japan, 1922, 1074) found that Taxine isolated from the leaves of yew (*Taxus baccata*) produced in the province of Hida is a white amorphous powder of bitter taste, m.p. 105°–111°, after sintering at 82°. Analysis confirmed the formula $C_{37}H_{51}O_{10}N$ previously assigned to the alkaloid; in 5 and 10 p.c. alcoholic solutions it has $[\alpha]^{18} + 32^\circ 20'$ and $+35^\circ$ respectively.

Two chloraurates were obtained, one, m.p. 90°–105° (decomp.), soluble in hot dilute hydrochloric acid, and the other,



m.p. 110° (decomp.), insoluble in hot dilute hydrochloric acid. When heated with 5 p.c. sulphuric acid, the alkaloid is partly decomposed, a compound reducing Fehling's solution being produced, which, however, has not the characteristics of sugar. Emulsin is without action on the alkaloid. When heated with alcoholic potash, taxine is decomposed into formic and acetic acids, an amorphous acid, m.p. 94°–95°, and molecular weight 215, a crystalline acid (perhaps cinnamic acid), m.p. 133°, and a compound, $C_{23}H_{33}O_4N$, m.p. 105°–110°, insoluble in dilute sulphuric acid. By bromination in glacial acetic acid, the alkaloid gave a tetrabromide, $C_{37}H_{51}O_{10}NBr_4$, a yellow, amorphous powder, whilst in dilute sulphuric acid solution, a tribromide, $C_{37}H_{52}O_{10}NBr_3$, a light yellow, amorphous powder, is formed (Chem. Soc. Abstracts, 1923, 124, i. 361).

The quantity of taxine which may be extracted from the yew, *Taxus baccata*, is apparently independent of the locality in which the tree is grown, though male trees contain on the average about twice the amount present in female trees. The boughs and young sprouts contain a very small amount. It has not yet been possible to obtain taxine, $C_{37}H_{51}O_{10}N$, in a crystalline condition. When distilled it yields a small quantity of cinnamic acid, and on distillation with zinc-dust, styrol is obtained. Nitric oxide passed into an ethereal solution of taxine produces a mixture of the nitrate and the nitrite. When methylated with methyl iodide a rather unstable methiodide is formed, m.p. 123°–125°. When treated with water or, better, with sodium hydroxide solution, this methiodide decomposes, forming trimethylamine and an amorphous compound of the formula $C_{35}H_{44}O_{10}$, fine white powder, m.p. 120°–140°, which on distillation or on treatment with acid yields cinnamic acid, and on oxidation with permanganate, benzaldehyde and benzoic acid, whilst by the action of sodium hydroxide solution in the cold, acetic and cinnamic acids and an insoluble product

are formed. Taxine itself, when treated with sodium hydroxide solution yields one molecule of acetic acid, a little cinnamic acid, and a basic amorphous compound containing nitrogen. If this compound, or taxine itself, is heated on the water-bath with 5 p.c. sulphuric acid for ten hours, a crystalline compound, $C_{11}H_{15}O_2N$, is obtained, hydrochloride, m.p. 173°–174° (decomp.). This compound yields on heating cinnamic acid and trimethylamine, and on oxidation benzoic acid and benzaldehyde, and is probably β -dimethylaminohydrocinnamic acid. The following formula is suggested for taxine:—



(E. Winterstein and A. Guyer, Zeitsch. physiol. Chem. 1923, 128, 175–229; cf. J. 1922, 230 A; J. Soc. Chem. Ind. Sept. 7, 1923, 856 A).

Toxicatin $C_{13}H_{22}O_7$, an inodorous slightly bitter substance, m.p. 166°–167°; when combined with 2 molecules of water its m.p. is 165°; $[\alpha]_D - 72.9^\circ$; is also found in *Taxus baccata* (Lefebvre, J. Pharm. Chim. 1907, 26, 241). See YEW.

TCHA-LAN. A blue powder containing copper; used by the Chinese for obtaining a blue colour on porcelain (Ebelmen and Salvétat, Ann. Chim. Phys. [iii.] 35, 338).

TEA. This term is usually understood to signify both the dried leaves of certain plants belonging to the natural order *Ternstroemiaceæ* (notably two species of *Thea*—*T. chinensis* and *T. assamica*, or of hybrids between these two); and also the aqueous infusion prepared from them.

Tea has been used in China for many centuries. Reference to it is said to have been made by a Chinese writer who lived 2700 years B.C. as well as in poems edited by Confucius, about 500 B.C. It appears at first to have been used only medicinally, but Yo Lu, a writer who lived during the latter part of the Tang dynasty, which lasted from 618 to 906 A.D., says that it was drunk in the sixth century, and that during the eighth century it became so common that a tax was levied on it. Arab writers speak of it in China in the ninth century, and it seems to have been introduced into Japan in 810, where its cultivation was commenced early in the thirteenth century. There was no knowledge of tea in Europe until after 1517, when intercourse began between Portugal and China. It was first brought to Europe in 1610 by Dutch merchants, and some years later was introduced into England. A Mr. Wickham, the agent of the East India Company in Japan, wrote to an officer-friend named Eaton, in 1615, asking for 'a pot of the best sort of chaw' (tea), and in Mr. Eaton's own accounts occurs the item, 'Three silver porringers to drink chaw in.' Pepys mentions having tasted it, and writes in his diary, 28th September, 1660, 'I did send for a cup of tee (a China drink), of which I had not drank before,' and, June 28th, 1667, 'Home and there find my wife making of tee, a drink which Mr. Pelling the Potticary tells her is good for her cold and defluxions.' The East India Company presented 2 lbs. of tea to Catherine, the Queen of Charles II., in 1664, and in 1669 they imported it directly from China. Garway, the first tea-dealer in London, issued in 1659 a

broad-sheet headed, 'An exact description of the growth, quality, and virtues of the leaf of Tea.' In 1660 he bought a lot, and sold it according to quality at from 15s. to 50s. per lb. He had the infusion 'made according to the directions of the most knowing merchants and travellers into those Eastern countries.' Much prejudice had to be overcome, however, before tea became a popular beverage in England, owing to the fashion of tea drinking being a foreign one, and Jonas Hanway, one of the leading opponents of the new custom, describes it, in his *Essay on Tea*, published in 1707, as 'pernicious to health, obstructing industry, and impoverishing the nation.' In 1666, there were not more than 100 lbs. of tea brought to Europe, and its price was as high as 60s. per lb., but about ten years later, the quantity imported from China by the East India Company had reached nearly 5000 lbs. By 1725, the price had fallen to from 13s. to 20s. for black tea, and to from 12s. to 30s. for green tea. In 1745 the amount brought to England alone was 730,000 lbs., and in 1800 the infusion had become a very general beverage in this country. The following table gives some idea of the growth of the consumption of tea in the British Isles, from the beginning of the last century to the present time (1923):—

Year	Amount consumed (lbs.)	Amount per head of population (lbs.)
1800	23 million	1.4
1850	51 "	1.8
1860	77 "	2.6
1870	118 "	3.7
1880	158 "	4.5
1890	194 "	5.0
1900	250 "	6.0
1910	287 "	6.3
1913	306 "	6.6
1914	318 "	6.8
1915	317 "	6.8
1916	302 "	6.4
1917	277 "	5.9
1918	310 "	6.6
1919	388 "	8.0
1920	392 "	8.1
1921	410 "	8.3
1922	411 "	8.4

The reduction of duty no doubt aided this rapid increase. From about 1833, when the monopoly of the East India Company was withdrawn, the high duty of 6s. or 8s. per lb. was gradually reduced until in 1865 it was only 6d. per lb. Mr. Goschen reduced it to 4d. in 1890, since when it has varied between 8d. in 1904, to 5d. in 1913, then raised to 8d. in 1914, and to 1s. per lb. in 1915, remaining stationary at this rate until 1922, when it was reduced to 8d. per lb., which is the rate of duty at the present time (1923). The sudden fall in the consumption of tea in 1917 was due to restrictions on certain imports, including tea, in consequence of the war. From 1919 onwards, a marked and progressive increase is noticeable in the amount of tea consumed per head of population.

(N.B.—The figures in the above table apply to Great Britain and the *whole* of Ireland.)

China and Japan were formerly the only main tea-producing countries, although the plant was known as far back as 1780 to be

growing in India. In 1788, Sir Joseph Banks pointed out the advantages that would follow from the cultivation of tea in India, and in 1820 Mr. David Scott sent leaves to Calcutta from wild tea-plants growing in the districts that Sir J. Banks had named as suitable for tea-planting; but owing to some doubt as to the true character of the leaves no action was taken in the matter.

Mr. C. A. Bruce noticed the tea-plant growing wild in the jungles of Assam, and in 1839 he received a gold medal from the Society of Arts for this discovery, and for successfully growing and preparing China tea in India. Mr. Bruce's right to this medal was disputed by Captain Charlton, who said that he had pointed out the indigenous Assam tea-plant in 1832. The honour of its discovery has also been claimed for Moneram Dewan, a native. Lord William Bentinck, when Governor-General, formed a committee to introduce the cultivation of tea into India; and in 1834 Dr. Wallish admitted that David Scott had been correct with regard to the leaf. The Government committee at first sent to China for seed and for skilled manufacturers, but Captain Jenkins again pointed out the indigenous *Thea assamica*, and this was used for some years.

In 1836, 1 lb. of tea was sent from India to London: in 1837, 5 lbs.; in 1838, 12 small boxes; in 1839, 95 boxes. In 1839 the Assam Tea Company was formed, which in 1840 bought one of the Government tea-gardens that had failed, and the cultivation has been carried on by private enterprise ever since. The Government however, was not satisfied with the amount of success attained, and a few years afterwards sent Mr. Robert Fortune to China to study the cultivation and manufacture of tea, and to bring seeds and plants thence to India. He found excellent tea grown and made in the Chusan Islands, and in the neighbourhood of Ning-po and of the Temple of Tein-tung, twenty miles inland; but as this was only for home consumption, he determined also to see and get seeds and plants from the districts of the interior, though this was forbidden to foreigners by Chinese law.

In 1849 he took his young tea plants to Hong Kong, and sent them in four different vessels to Calcutta. In April, 1850, he returned to Shanghai and the north to get implements and engage manufacturers to accompany him. Altogether he introduced more than 12,000 plants into India, and went carefully over the chief tea districts there, travelling up the Ganges and beyond Allahabad. The plantations over the principal tea districts there lay about 29° and 30° N. lat. and 78° and 79° E. long. and were chiefly in the neighbourhood of Almorah, situated about 4000 and 5000 ft. above the sea. The principal districts now are: Upper and Lower Assam, Bheel Cachar, Chota Nagpore, Chittagong, Darjeeling, Dooars, Dehra Doon, Neilgherry, Sylhet, Terai, and Travancore.

Although in India the native plant or a hybrid is now used (*v. Cultivation*), Fortune's introduction of Chinese growers and manufacturers to teach methods to the natives must have greatly aided the Indian industry.

The rapid increase in the amount of Indian tea imported into England may be seen from the fact that in 1857 we received from India only

121,000 lbs., whilst half a century later the amount was over 150 million lbs. In 1889 the supply of Indian tea to the United Kingdom for the first time exceeded that from China, which was also surpassed by Ceylon tea in 1891, and the excess has been maintained ever since, with a corresponding diminution in the importation of China tea.

Many attempts at the cultivation and manufacture have been made in Ceylon. In 1868, the coffee plants were diseased and the crop failed, and attention was therefore turned to the cultivation of other crops suitable to the climate as cacao, cinchona and tea. The latter industry has grown enormously, as may be seen from the table below.

Ceylon tea combines some of the good qualities of Indian and of Chinese tea, and it does not require blending, but it does not keep so well. In this respect Chinese tea is much the best, and it is customary therefore to store smaller quantities of Indian or Ceylon tea than of Chinese. In comparison with Indian tea, Chinese is also more uniform in quality. Some Indian and Ceylon growers are apparently inclined to attend more to quantity than to quality. Our increased importation from India and Ceylon is partly owing to the heavy transit and export duties levied on tea by the Chinese Government, also to the faulty and often objectionable methods of manufacture, chiefly by hand labour, followed in China, as compared with the more scientific methods and almost universal employment of machinery in India and Ceylon.

IMPORTS TO THE UNITED KINGDOM
(In million lbs.).

—	China	India	Ceylon	Other countries	Total
1873	135	20	(23 lbs.)	8 ³ / ₄	163 ³ / ₄
1875	170	26	(1400 lbs.)	1 ¹ / ₂	197 ¹ / ₂
1880	158 ¹ / ₄	45 ¹ / ₂	(150,000 lbs.)	3 ¹ / ₄	207
1885	140	64 ³ / ₄	3 ³ / ₄	4	212 ¹ / ₂
1890	69 ¹ / ₄	100 ¹ / ₂	47	6 ³ / ₄	223 ¹ / ₂
1895	40	123 ¹ / ₂	83 ¹ / ₂	8 ¹ / ₂	255 ¹ / ₂
1900	21 ¹ / ₂	153 ¹ / ₂	114 ¹ / ₂	9 ¹ / ₂	299
1905	7 ³ / ₄	179	106 ¹ / ₄	15 ¹ / ₂	308 ¹ / ₂
1910	19	180 ¹ / ₄	107 ¹ / ₂	25	331 ³ / ₄
1913	16 ¹ / ₄	203 ¹ / ₂	111	34 ¹ / ₄	365
1914	21 ³ / ₄	203 ¹ / ₄	110	37	372
1915	36 ³ / ₄	228	123 ¹ / ₄	43	431
1916	20	215 ¹ / ₄	107 ¹ / ₂	35	377 ³ / ₄
1917	8 ¹ / ₄	148 ¹ / ₄	78 ¹ / ₂	10 ³ / ₄	240 ³ / ₄
1918	1 ¹ / ₂	373	88 ¹ / ₂	0 ¹ / ₂	463 ¹ / ₂
1919	26 ¹ / ₂	287	137 ¹ / ₄	43 ¹ / ₂	494 ¹ / ₄
1920	16	250 ¹ / ₄	123 ¹ / ₄	41 ¹ / ₂	431
1921	4 ¹ / ₂	286 ¹ / ₂	118 ³ / ₄	37 ³ / ₄	447 ¹ / ₂
1922	11	255 ¹ / ₄	111 ¹ / ₂	41 ¹ / ₄	419

From the above table it will be seen that the rapid increase in the imports of Indian and Ceylon tea was arrested during the period 1905–1910, whilst the importations from China and other countries showed a marked tendency to increase. This is due partly to the fact that Indian tea is gradually displacing China tea in markets such as Russia,

the United States, and Canada, hitherto favourable to the teas of China and Japan, so that the supply of Indian tea is at present barely equal to the demand. In Ceylon, moreover, a considerable amount of tea has, in recent years, gone out of cultivation for the more profitable cultivation of rubber. Also, the Chinese have been making strenuous efforts to regain some of their lost trade by fiscal changes and by attention to improved methods of cultivation and manufacture. The returns after 1910 showed a revival of the Indian and Ceylon tea trade with the United Kingdom up to 1915, then a rapid falling off to 1917, when, as a war measure, the importation of tea was prohibited, except under licence.

The European nations who consume most tea are Great Britain, Holland, and Russia. Next to Great Britain, the United States import more than any other country, but reckoned by the amount drunk per head the people of Australia and New Zealand are the greatest tea-drinkers in the world.

Europe is supplied chiefly by China and India, and North America by Japan; but China black tea and Japan green tea are being rapidly supplanted in Canada and the United States by Indian black and Ceylon green tea respectively.

The methods of making the infusion vary in different countries. In China a pinch of tea is put into the cup, boiling water is poured on it, and the infusion is drunk at leisure, even after it is cold, and without milk or sugar. The water to make it is got from a running stream if possible, otherwise from a spring, *not* from a well, and is boiled slowly. The methods prevailing in Japan are described further on. In England the old fashion of letting the tea ‘brew’ and constantly adding hot water to the same leaves, is dying out; and the best tea-makers pour boiling water on to the leaves, which have been put into a heated pot, let it stand on them for about five minutes, and then pour off the infusion or take out the leaves. The reason for this method is, that by that time most of the theine and essential oil, but not more than a third of the astringent tannin, have been extracted. In Russia, lemon-juice is added to the infusion. In Germany, rum is sometimes added, as well as cinnamon or vanilla. In Spain, lemon-verbena leaves are added.

Botany. The tea-plant (*Thea assamica* or *Camellia Thea*) belongs to the order *Ternstræmiaceæ*.

Leaves.—Lanceolate, serrate, acute, and thick. They are alternate, and their stalks are short. Their upper surface is green and glabrous, and their under surface sometimes hairy on the nerves. The veins from the midrib go nearly to the edge, and then unite to form an intra-marginal vein. The leaves are dotted with pellucid oil glands, and numerous unicellular hairs are found on the under surface, especially of young leaves. The hairs, after emerging from the epidermis, bend suddenly at a right angle in a direction parallel to the surface of the leaf, and are very characteristic. The stomata are very numerous and are bordered by two special cells of reniform shape. Stellate crystals of calcium oxalate occur in the internal tissues or mesophyll, as well as thick-walled

sclerenchymatous cells of very irregular shape giving support to the upper and lower layers of the leaf, and known as 'sclerites' or 'idioblasts.' These serve to distinguish tea from most other leaves likely to be used for the purpose of adulteration.

Flowers.—White or slightly yellow, or rose tinted, axillary, regular and hermaphrodite. Bracts, two or three below the calyx. There are five round and convex sepals, and five obovate obtuse petals (more rarely, six or more). The stamens are indefinite, monadelphous, and adhere to the petals by their base. The styles are three in number, with simple stigmas. The ovary is superior and three-celled, each cell containing from four to five pendulous anatropous ovules.

Fruit.—Woody, forming a three-celled loculicidal capsule, which remains green for a long time. Each cell contains one exalbuminous seed, the remaining ovules never ripening.

Cultivation. Our chief authority on the cultivation and manufacture of tea in China is Robert Fortune, who in his *Journey to the Tea Countries of China* gives many interesting particulars about the cultivation and manufacture of tea, and of his adventures in getting to the interior disguised as a mandarin.

He states that the parts of the world best suited by climate for the cultivation of the tea plant are China, Japan, India, Ceylon, South America, parts of Australia, the shores of the Mediterranean, the middle of France, and even Ireland. Java is now one of the chief tea producing countries, and amongst other countries where tea is more or less successfully cultivated at the present time may be mentioned Burmah, the Straits Settlements, Natal, Nyassaland, Mauritius, Queensland, the Fiji Islands, Brazil, the Azores, and the Caucasus.

A warm climate is essential. In the most favourable districts in China the ordinary range of the thermometer in the summer at 3 p.m. is between 80° and 90°F.; it sometimes reaches 100°, and it rarely falls below 32° in winter.

The best position for a tea-plantation, if other conditions are favourable, is a slope facing the south, because on sloping ground there is natural drainage, and the soil does not get too wet; it ought never to be as wet as in rice-fields. If flat ground is used, the tea-gardens are often artificially raised, and are always carefully drained. The spring rains are most beneficial, provided the drainage be efficient. There must be a constant supply of water, either from natural sources or by irrigation. Hilly districts are suitable, because the vegetable matter washed down from above enriches the gentler slopes and the level ground below. Increased altitude (within limits) appears to improve the flavour of tea, but with a diminution of the quantity of leaf produced. The plant flourishes best in rich loam mixed with sand and gravel. Oak-bearing land is considered extremely good for tea plants.

The seed—which is in appearance like a hazel nut, having an outer and an inner shell inclosing a kernel, and ripens about a year after the flower has faded—is gathered in October, and kept in sand and earth, in which it germinates, until March, when it is sown in rows. Holes are dug and left for about two weeks, then filled with

surface soil, and three seeds are put into each hole about six inches apart. The best plant remains in the hole, and the others are transplanted to vacancies. The plants are about 4 ft. apart, and the same distance separates the rows. About 26 lbs. of seed are required for an acre, yielding about 2500 shrubs. Sometimes the seeds are sown more thickly in corners of the tea-farm or in nurseries, and the plants transplanted when a year old at the beginning of the rainy season.

The wild plant (originally, probably, the *Thea assamica* of the forests of Northern India) may grow to a height of from 30 to 50 ft., but the cultivated plants are pruned and kept to a height of from 3 to 6 ft., so that they become well-spread, bushy shrubs resembling somewhat the 'Portugal laurel' in appearance. The leaves are not picked until the plant is three years old. It does not yield its full quantity until its sixth or seventh year, and in China, leaves are seldom gathered from a plant more than twelve years old. A good cultivator takes care that some portion of his farm shall be resown every year.

In India, only those plants are allowed to flower which are to be kept for producing seed, the leaves of which are not to be made use of. Fortune introduced Chinese seed into India; but it has been found that the indigenous plant, or a cross between it and the Chinese varieties, yields better tea in India. The Chinese plant makes the best green tea, whilst hybrids are best for black. Only such seeds as are used in India are imported into Ceylon.

The raw leaves yield only about one-fifth of their weight of manufactured tea. The plants give in their third year not more than a *maund* (80 lbs.), but in their fifth year about 280 lbs. of tea per acre. The amount increases from the fifth to the twelfth year, but varies greatly in different districts, and it also depends on the plucking, whether 'fine' or 'coarse.' In the richest years, the amount in some places (e.g. Sylhet) may reach 1000 lbs. per acre. A tea bush from 8 to 22 years old will yield $\frac{1}{4}$ lb. of manufactured tea, and taking 2500 bushes per acre, the average yield in India is thus over 600 lbs. per acre.

Manufacture. The two great classes of tea are *green* and *black*, the differences between them depending solely on the mode of manufacture. Sub-divisions depend on the *age of the leaves*, i.e. the time of the year they are gathered, and the *way they are rolled*.

The chief sub-divisions are as follows:—

Green Varieties.

Hyson.—Leaf-buds and first leaf; picked in April. The young leaves, which are very uniform in size, are carefully twisted and rolled longitudinally into spiral form.

Skin Hyson consists of the inferior leaves of Hyson rolled transversely and longitudinally and frequently enclosing the debris of other green teas. It is often merely tea refuse, and the coarser kinds are known in the vernacular as 'tea bones.'

Gunpowder.—According to Dujardin-Beaumez, this is simply carefully selected hyson. According to Johnston and Church, it is from a

special plantation, and flavoured with *Olea fragrans*, the sweet-scented olive. The leaves are cut transversely in three or four parts before being rolled into pellets.

Pearl or Imperial.—Dujardin-Beaumetz describes this as a kind of hyson, but coarser than the true hyson, and of a silver-green colour. Johnston and Church say that the true Imperial, which is excellent, is rarely sent to Europe, and that what we call 'Imperial' is a tea from the Chusan Archipelago flavoured with the *Olea fragrans*. The tea occurs in the form of pellets made by rolling the leaves first longitudinally, then transversely.

The quantity of green tea consumed in this country is only one-sixteenth of 1 per cent. of the whole, or 250,000 lbs. out of a total consumption of 408,000,000 lbs., and of this only a small proportion is faced.

Black Varieties.

The different kinds of black tea are usually classified according to the age of the leaf. The youngest leaves give the best tea, and the order, commencing with the youngest when plucked, is as follows:—

(a) <i>Flowery Pekoe</i>	} 'Poco' refers to the white down of the young leaf.
(b) <i>Orange Pekoe</i>	
(c) <i>Pekoe</i>	
(d) <i>First Souchong</i>	} 'Souchong' means 'small plant.'
(e) <i>Second Souchong</i>	

(f) *Congou*.—'Congou' means 'labour,' and is intended to express the great care required in the preparation of this tea. (a) (b) (c) mixed make *Pekoe*; (d) and (e) mixed with (a), (b), (c) give *Pekoe-Souchong*.

Pekoe.—Youngest leaf and leaf-buds; picked in April. This is sometimes flavoured by the addition of orange, rose, or jasmine flowers. When with the first-named, it is called *Orange Pekoe*.

Souchong.—The strongest and perhaps finest of the black leaf teas. It consists of the larger of the young leaves, and is suitable for use either alone or in blends.

Congou.—The younger leaves from the third crop, older and larger than *Souchong*. This constitutes the ordinary beverage of the inhabitants of China and Russia.

Bohea.—The commonest variety of tea, consisting of the older leaves of the third crop or a mixture of various leaves, stalks, and dust.

Caper (plain-scented).—Various teas or tea-dust made into hard grains by means of gum or rice-water, sometimes polished with graphite or coloured with indigo, &c.

Broken Pekoe.—Siftings of various Pekoes.

Fannings.—Siftings of Congou.

There are other special varieties of teas as Twankay (green), Kaisow (red leaf), Moning and Oolong (black, with more or less of the flavour of green), used chiefly for giving 'life' to blends.

The leaves are plucked three times a year. In April (that is in China just before the spring rains); at the end of May or beginning of June; and towards the end of June, or, according to some authorities, in July. Sometimes there is a fourth gathering in the late summer or early autumn, but leaves of such a size and age as they are then make only the common and coarser kinds of tea. In South Australia there are always four, and sometimes in wet seasons

a fifth gathering. Women are generally, if not always, employed in India, and sometimes in China, for the picking.

The plants are picked as successive 'flushes' appear, a 'flush' being the throwing-out of new shoots and leaves; and the number of flushes in a season—that is, in from seven to nine months—varies from 18 to 25, according to the soil and climate. In Ceylon, the flushing continues all the year round. Up to a certain point the more a plant is picked the more new shoots it throws out. At the end of the season each shrub is 3½ or 4 ft. high, and about 5 ft. in diameter. It is then pruned down to a height of 2 feet and a diameter of 3 ft., and thus it remains until the spring.

In the manufacture of *green tea* the object is to keep the colour and prevent fermentation; it is necessary, therefore, to roast as soon as possible after picking, and finish the whole process quickly.

In the manufacture of *black tea*, on the contrary, the leaves are dried slowly before manipulation, and one of the processes is that of fermentation (*cf.* Eighth Int. Cong. Appl. Chem. 1912, Sect. VIII.).

Processes of manufacture of green tea. Chinese methods.

The methods and apparatus employed in China are very simple and primitive. The tea farms are very small, seldom exceeding five acres, and almost every cottager grows sufficient tea to supply the wants of his family and possibly secure other necessities of life by selling the surplus to the travelling tea-merchants who periodically visit the country districts for that purpose.

The principal processes are as follows:—

Steaming.—To get rid of the raw flavour, and preserve the colour, the leaves are spread out in bamboo trays and fitted into a bamboo box, the bottom of which is a boiler. Here the leaves remain for an hour or two. They then are exposed on tiled floors, or in shallow bamboo trays out of doors in the shade, to prevent their turning yellow and becoming hard and brittle by drying too rapidly as they would if placed in the sun, and are meanwhile separated from stalks and dirt.

Roasting.—Half a pound of leaves at a time are put into a *kno* or iron pan, 10 ins. deep and 16 ins. in diameter, which is set in a brick stove over a brisk wood fire. Here the leaves are kept 4 or 5 minutes, and stirred rapidly with the hand. When taken out they are moist and flaccid, although much vapour has been given off.

Rolling.—The object of this is to break the cells, contents of which come out and spread over the surface of the leaf, so that a fine aroma is produced. This is done on the rattan table, where the leaves are rolled by hand into balls, shaken out again, and rolled once more, passing from hand to hand until they reach the head workman, who sees whether they have the proper twist. If they are right they are shaken out on flat trays or sieves, and allowed to cool for a few minutes.

The second roasting is done over a slow charcoal fire for an hour or an hour and a half, at the end of which the green colour is fixed, dull at first, but gradually growing brighter. During

the second roasting one man moves and occasionally rolls the leaves, while another fans.

Sifting.—This is first done by means of sieves of different sizes; then the leaves are winnowed on large bamboo trays, and finally they pass through the winnowing machine. This gets rid of dirt and impurities, and separates the different kinds of tea, according to size and twist of leaf.

During the sifting the leaves undergo a *third roasting* or *re-firing*. It was about 5 minutes before the end of this last roasting that the manufacturer used to add the Prussian blue, &c., for colouring. This was done for the foreign market only, as this highly coloured tea was prized in Europe until it was discovered to be faced. The whole manufacturing process takes about 10 hours. Sometimes the sorting and re-firing take place at Canton before exportation instead of in the interior.

Japanese methods.

The principal kinds of Japanese green tea are Gyokuro and Sencha, which are those chiefly used by the Japanese themselves, and exported to the United States of America, Canada, and Australia.

The methods of manufacture are very much the same as in China, but whilst machinery is now almost universally employed in Japan for teas intended for exportation, yet owing to a prevalent idea that the use of machinery is detrimental to the development of the finest aroma, the superior qualities of tea are still prepared by the old-fashioned hand processes.

Indian methods.

Machinery is used almost exclusively in India for the manufacture of tea, as ensuring 'more cleanliness and uniformity' than the method by hand. Each process appears to be gone through once without necessity for repetition.

There seems to be less difference between the Indian and the Chinese mode of manufacturing green tea than there is between the methods of the two countries in making black. The Indian method of making green tea is as follows:—

The leaves are picked twice a day. Those which are brought in at 1 p.m. are partly manufactured the same day; those which come in at night are spread six inches thick until next morning. The various process are:

1. *Drying* (if necessary).

2. *Roasting.*—This is done in pans over fires until the temperature is 160° F., and the leaves are meanwhile vigorously stirred for seven minutes.

3. *Rolling.*—This is done four times in succession, the leaves being dried in the sun between each rolling.

4. *Second roasting.*—The leaves are returned to the pans, and roasted at the same temperature as before.

5. *Beating.*—Bags are filled with the leaves, which are then beaten heavily. They remain in the bags all night.

6. *Third roasting.*—During the stirring this time the temperature gradually falls from 160° F. to 120° F.

7. *Sifting and sorting.*—The sieves are round

and made of brass wire or cane, with wooden sides 3½ ins. high. Before sifting, any red leaves there may be are carefully picked out.

The method of manufacture in *Ceylon* is the same as that in India.

Processes of manufacture of black tea.

Chinese methods.

A little of the soft stalk is picked with the young leaves and leaf-buds for black tea.

Withering.—The leaves are spread on large bamboo trays or mats, and exposed out-of-doors for some hours. If leaves are gathered during the wet season, this first drying takes place indoors on frames standing some feet above pans of hot charcoal. This process renders the leaves soft and pliable; the stalks bend without breaking, and do not crackle when compressed.

Tossing and fermentation.—In a cool building, or in the shade out-of-doors, the leaves are then tossed and gently patted till they are soft and flaccid. They then lie in heaps, covered with a cloth, and are carefully watched until they get a slightly reddish tinge, and give out a fragrant smell.

First roasting and rolling.—This roasting is for 5 minutes in shallow iron pans over wood fires. The rolling is on rattan tables, the same as for green tea. Sometimes the rolling takes place first, and sometimes the roasting.

Exposure out-of-doors.—The leaves are now shaken out thinly on sieves, and put out-of-doors on bamboo frames for about 3 hours. In the black-tea districts they are seen in front of all the cottages; and workmen go from one to another turning and separating the leaves. The day should be fine and dry, but not too hot. When dry enough, they are removed to the factory.

Second roasting and rolling.—This roasting is in the same shallow iron pan as before, and the rolling on the same table.

Drying and rolling.—The leaves are spread to a depth of about 1 in. in sieves, and these are put into tubular baskets called poey-longs, which are slightly contracted in the middle, and are 2½ ft. long and 1½ ft. broad, somewhat like a dice-box in shape. There are cross-wires a little above the contraction of each basket on which the sieve stands. The poey-long, the mouth of which is covered by a bamboo tray, stands upright over a low stove built on the ground, and contains a small quantity of charcoal, so that the tea-sieve is about 14 ins. above the stove. These stoves are built round three sides of a long narrow room, and are 2 or 3 feet deep, and 5½ ins. high. While the rolling goes on, the balls of leaves are left standing in heaps until all are done. The drying and rolling go on alternately, either two or three times, until the leaves are dry and crisp and have the right dark colour.

Sifting.—This is done by means of large circular bamboo trays, and the large leaves, if necessary, are picked out by hand.

Final drying.—The fires are covered to reduce the heat. The leaves are placed much more thickly in the baskets, and the workman makes a hole with his hand through the centre of those in each sieve, to equalise the heat and allow the charcoal vapours to escape. Here the

leaves remain over a slow fire for 2 hours or longer. The mouth of the basket is quite closed by a tray. For home consumption in China, tea is not dried quite so much, and it is kept for a year before use.

Japanese methods.

The manufacture of black tea in Japan has not hitherto been very successful, owing probably to imperfect fermentation, a process to which the native leaf does not appear to be so well adapted as the China leaf.

The mode of manufacture is the same in principle as that of China, but differs in the order of the processes and the time of their duration.

Large quantities of tea of the Oolong variety are shipped from Formosa. This, although similar in appearance to black tea, has the flavour of green tea.

All teas in Japan are re-fired in the 'go-downs' of the exporters. This is to drive off any excessive moisture, tea being extremely hygroscopic, and to destroy any germs which might, especially in the presence of moisture, cause the tea to decay on its voyage to other parts of the world. According to Kozai, the amount of moisture in ordinary Japanese tea is from 10 to 11 p.c., but it is reduced by re-firing before exportation to 3 or 4 p.c.

It has been proved by experiments with leaves of other plants in Japan that steaming not only preserves their colour but prevents fermentation. This may be because the heat of the steam destroys the enzymes which produce fermentation. Hence, for black tea, the leaves must on no account be steamed, but withered, and then allowed to ferment. For green tea the leaves are steamed to prevent fermentation and preserve colour, and are manufactured quickly.

In Japan, other kinds of tea are manufactured exclusively for home consumption, called respectively *bancha kamairii* or *pan-roasted tea* and *yencha* or *flat tea*. The former is a very inferior tea consisting of old leaves from the last year's crop mixed with broken stalks and twigs. Kamairii is made simply by alternate roasting in an iron or bronze pan, and rolling on a table seven or eight times over. Until 250 years ago all tea was made so, but now it is rare. According to Y. Kozai this is sometimes made in China, and is known there as '*sencha*' (*v. supra*). For *flat tea* the leaves are supplied from a special plantation. They are not rolled or touched by the hand at all, but are spread on stiff paper for firing by means of bamboo sticks, and are alternately collected and spread out until nearly dry. Then they are taken from the furnace, all the broken or yellow leaves removed, and fired again. The final drying lasts all night at a gentle heat, and the leaves are then separated into three classes. For use they are ground to a powder of the fineness of flour, drunk with the infusion. This tea ('yencha') is usually reserved for ceremonial occasions.

Indian methods.

The processes are as follows:

1. *Withering* on fine basket-work trays in the sun.

2. *Rolling*. This is done either by the rolling machine or by a line of men on each

side of a table, who pass the leaves from one end to the other. When soft and 'mashy,' and giving out juice, the leaves are made into a ball, the juice that has come out being mopped up constantly during the process.

3. *Fermentation*. The balls stand until fermented, and are most carefully watched, as the flavour and quality of the tea depend largely on stopping this process at the right moment, and only skilled tea-makers can judge of this. At the proper time the balls are broken up, and the leaves spread thinly on mats in the sun. When they get rather black they are collected and re-spread, so that all the leaves may be alike, but this does not take long, for

4. *Drying or Firing* should take place as quickly as possible after the fermenting process, to drive off all the moisture. This is generally done in a chest of firing drawers, which consists of a set of trays one above the other, the bottom of each, on which the leaves are spread, being made of fine wire gauze, so that all the trays can be heated at once. Formerly charcoal fires always produced the heat, but now hot air is often used instead. When the tea comes out of this machine it is almost black, and has a very delicate aroma.

5. *Sorting*. In sieves to separate the leaves into the different kinds for commerce.

Chemistry of tea. The analyses of air-dried tea differ according to whether the tea be green or black, where it has been grown, and other circumstances.

The most important constituents of tea are caffeine (theine), tannin, ash, and essential oil. Of these it is generally found that there is rather more caffeine in black tea than in green, and more tannin in green (though this rule is not without exceptions); the amount of ash is fairly constant; the quantity of essential oil is very small in both, but it seems to be larger in green tea than in black. The total matter soluble in hot water is also larger in green tea than in black.

The pure tannin of tea may be obtained in the following way: Fresh tea leaves dried at a moderate temperature are powdered and extracted with benzene to remove chlorophyll and resins. The residue is extracted with hot 80 p.c. alcohol, the solvent distilled off, and the syrupy residue treated with water containing a few per cents. of sodium chloride. After filtering from insoluble matter the solution is extracted with ether to remove gallic acid, and then with ethyl acetate to remove the tannin. The tannin solution is dried over sodium sulphate, concentrated *in vacuo*, and poured into chloroform. The precipitated tannin is filtered off quickly and purified by re-solution and re-precipitation with ethyl acetate and chloroform. The pure product is white, and oxidises in air to a brown syrup. It dissolves readily in water, methyl alcohol, ethyl alcohol, acetone, aniline, and acetic anhydride; less readily in ethyl acetate, acetic acid, and sulphuric acid; and is insoluble in chloroform, benzene, carbon bisulphide, and dry ether. Analysis and molecular weight agree with the formula $C_{20}H_{20}O_9$. With ferric chloride it gives a blue-black precipitate or coloration, with lead acetate a buff-coloured precipitate, with bromine in aqueous solution a yellow precipitate. Permanganate oxidises the tannin

completely to carbon dioxide, and nitric acid oxidises it to oxalic acid; it reduces Fehling's solution, gives a yellow precipitate with phenylhydrazine, and reduces an ammoniacal silver solution. On boiling for some hours with dilute sulphuric acid an insoluble red precipitate is formed. On warming with acetic anhydride and sodium acetate, tea tannin yields an acetylated product of the formula $C_{36}H_{38}O_{17}$. It is assumed therefore that the tannin has 8 hydroxyl groups apparently of phenolic character, one ketonic group, and no carboxyl group (J. J. B. Deuss, Rec. trav. chim. 1923, 42, 496-498; J. Soc. Chem. Ind. 1923, 42, 793 A).

The tannin from tea is included amongst Freudenberg's 'condensed tannins' (Chemie der natürl. Gerbstoffe, 1920, 5), both on account of its precipitation by bromine, and of its formation of reddish-brown insoluble products by oxidation and with dilute acids. It is not attacked by oxidising enzymes. It is best identified by means of the blue colour produced with ferric chloride, which changes to green with excess of the reagent. An aqueous solution of tannin from tea spontaneously deposits a brown substance, soluble in excess of the tannin solution. Similarly, a dark red substance is obtained by the action of dilute acids, but this is insoluble in excess of tannin solution (J. J. B. Deuss, Rec. trav. chim. 1923, 42, 1053-1054; J. Soc. Chem. Ind. 1923, 42, 1235 A).

A valuable paper by Y. Kozai (Researches on the Manufacture of Various Kinds of Tea: Bulletin No. 7 of the Imperial College of Agriculture and Dendrology, Japan) gives analyses of the tea-leaves (all of the same kind) from a certain plantation under three different conditions:—

1. Dried at 85° C.
2. Made into green tea.
3. Made into black tea.

The following are the results:—

	Original leaves dried	Same made into green tea	Same made into black tea
Crude protein . . .	37.33	37.43	38.90
Crude fibre . . .	10.44	10.06	10.07
Ethereal extract . .	6.49	5.52	5.82
Other nitrogen-free ext.	27.86	31.43	35.39
Ash	4.97	4.92	4.93
Caffeine	3.304	3.200	3.300
Tannin (calculated as gallo-tannic acid) .	12.91	10.64	4.89
Soluble in hot water .	50.97	53.74	47.23
Total nitrogen . . .	5.973	5.989	6.224
Albuminoid nitrogen .	4.107	3.937	4.106
Caffeine nitrogen . .	0.956	0.926	0.955
Amino nitrogen . . .	0.910	1.126	1.163

100 parts of dried leaves yielded:—

Green tea 98.64
Black tea (after fermentation) . 95.47

From the above figures it follows that in the process of manufacture the change in the amounts of the various constituents was such as is shown in the following table, where (+)

denotes the gain, (—) the loss in 100 parts of each constituent:

	Green tea	Black tea
Dry matter	— 1.36	— 4.56
Crude protein	— 1.70	— 0.61
Crude fibre	— 4.98	— 7.94
Ethereal extract	— 16.18	— 14.33
Other nitrogen-free extract	+ 11.31	+ 21.21
Ash	— 2.42	— 3.01
Caffeine	— 4.49	— 4.92
Tannin	— 18.67	— 63.82
Soluble in hot water . .	+ 5.96	— 11.69
Total nitrogen	— 1.08	— 0.61
Albuminoid nitrogen . .	— 5.57	— 4.58
Caffeine nitrogen	— 4.49	— 4.92
Amino nitrogen	+ 22.75	+ 22.42

The loss in ethereal extract is considerable, because part of the tannin changes during manufacture to a form insoluble in ether. In black tea, however, which undergoes fermentation, acids are formed during the fermentation that are soluble in ether.

The slight loss of ash and of caffeine arises from the mechanical loss of sap during manufacture.

The loss of tannin occurs during the heating processes in the manufacture of both kinds of tea. In black tea there is loss also during fermentation, when the tannin decomposes into substances *insoluble* in hot water. This accounts for the fact that hot water extracts less tannin from black than from green tea, and to this is no doubt largely due the preference given in the United Kingdom to black tea on the assumption that it is more wholesome than the green varieties.

Altogether, the change from the original leaves is greater in black tea, because of the process of fermentation.

The following are general analyses showing the differences between green and black tea:—

GENERAL ANALYSES (Bell).

	Congou (black)	Young Hyson (green)
Moisture	8.20	5.96
Caffeine	3.24	2.33
Albumin (insoluble) . .	17.20	16.83
Albumin (soluble) . . .	0.70	0.80
Extractive by alcohol containing nitrogenous matter . .	6.79	7.05
Dextrin or gum	—	0.50
Pectin and pectic acid . .	2.60	3.22
Tannin	16.40	27.14
Chlorophyll and resin . .	4.60	4.20
Cellulose	34.00	25.90
Ash	6.27	6.07
	100.00	100.00

ANALYSIS OF SIX VARIETIES OF CHINA GREEN TEA (Geissler).

	Max.	Min.	Average
Moisture	7.78	5.39	6.43
Half-hour extract . . .	44.70	30.20	36.74
Total extract	50.00	43.30	46.56
Insoluble leaf	49.61	44.60	47.05
Tannin	19.11	11.87	14.57
Caffeine	2.86	1.52	2.02
Soluble ash	5.02	2.02	3.28
Insoluble ash	6.38	2.11	3.61
Ash insoluble in HCl . .	0.66	0.21	0.49

would be between the leaves of plants grown under the usual conditions and those of plants screened from the light by wooden frames during the last three weeks of their growth before picking. He obtained the following results :—

	Screened leaves	Leaves exposed to light
Caffeine .	4.532 p.c.	3.784 p.c.
Total nitrogen .	7.835	6.954
Caffeine nitrogen .	1.311	1.0943
Tannin	no difference.	

The screened leaves were bleached, and had a fine and peculiar aroma.

Kozai states that there is not actually more caffeine in the screened than in the exposed leaves ; but that in the latter there is a preponderance of woody fibre which makes the total dry matter larger.

3. *Age of plants.*—It has been said that old plants make the best tea. This has not yet been thoroughly proved, but researches by O. Kellner with M. Tanaka and B. Minari on plants aged 4, 7, 16, and 20 years respectively, show that the amount of water decreases regularly with the age of the plant, and that all other changes are extremely irregular. The older the plant, the more manuring and pruning are necessary to get a good crop of leaves.

4. *Manuring* appears to have little effect on the chemical composition of the leaves, although it increases the number on each plant. Bush prunings, weeds, and general rubbish make good manure. Animal manure must be used with great care.

Theine or *caffeine* may be considered the active principle of tea, physiologically speaking, since it has been found in nearly all of the various plants whose leaves are used for infusions and take the place of tea.

The published determinations of caffeine in tea vary greatly, but this is partly owing to the different methods used.

Determinations of caffeine made in the Inland Revenue Laboratory (Bell's Foods) gave

Kind of tea	Price per lb. s. d.	Percentage of caffeine
Bohea	1 7	3.31
Congou	2 6	2.93
Young Hyson . .	3 2	4.29
Gunpowder low .	2 6	3.18
„ good	5 0	4.98
Assam, (low) . .	2 8	3.03
„ good	4 6	4.83

It will be seen that there is no direct relation between the proportion of caffeine and the commercial value of the tea.

Estimation of caffeine in tea.—Waage has examined 37 methods proposed or used for the determination of caffeine, but gives the preference to that of Mulder with certain modifications. This consists in treating the concentrated aqueous infusion by lime or magnesia, evaporating to dryness and extracting the caffeine with chloroform, ether, or benzene. In some cases the aqueous extract is first treated with lead acetate to remove tannin and colouring matters, the excess of lead being removed by sodium phosphate or hydrogen sulphide.

According to Blyth, low results may be obtained through loss in drying the extracted

caffeine by prolonged heating at 100° C., owing to the fact that caffeine sublimes below this temperature.

DETERMINATION OF CAFFEINE IN CEYLON AND INDIAN TEAS (PAUL).

	Elevation at which grown	Moisture per cent.	Caffeine p.c.	
			Original tea	Dry tea
<i>Ceylon teas.</i>				
	Feet			
Penrhos	2,500	6.8	4.56	4.89
F. L. C.	—	6.0	4.56	4.85
Nahalma	300	5.6	4.54	4.80
Hairs from leaves	—	6.6	2.40	2.57
Hardenhuish Pekoe	3,500	3.8	4.08	4.24
Woodstock Pekoe Souchong	4,200	3.6	3.44	3.57
Radilla Broken Pekoe	4,800	4.6	4.10	4.30
Morton Pekoe	400	4.2	3.98	4.15
Penrhos Broken Pekoe	2,500	6.4	4.64	4.96
Strathellic Orange Pekoe	2,000	5.4	4.10	4.33
Nahalma Orange Pekoe	300	5.4	4.06	4.29
Venture Orange Pekoe	4,300	5.4	3.74	3.95
St. Leys Pekoe Dust	4,600	5.6	3.46	3.66
Venture Pekoe Souchong	4,300	4.8	3.40	3.57
Venture Broken Orange Pekoe	4,300	6.6	3.98	4.26
Calsay Pekoe Souchong	5,000	6.2	3.22	3.43
Venture Pekoe	4,300	5.6	3.48	3.68
St. Clair Orange Pekoe	4,200	4.6	3.90	4.09
<i>Indian teas.</i>				
Pekoe Tips, picked out	—	7.56	4.27	4.62
Broken Pekoe	—	7.00	4.48	4.81
Pekoe	—	6.40	4.16	4.44
Orange Pekoe	—	4.80	4.66	4.89
Pekoe	—	5.60	4.48	4.74
Broken Pekoe	—	4.80	3.76	3.95
Pekoe	—	5.40	3.66	3.86
'Weak' Tea	—	6.80	4.06	4.35
'Strong' Tea	—	5.80	4.18	4.43
Mixture	—	6.00	3.64	3.87

Tannin.—The methods for the estimation of tannin are very numerous. That usually employed is Löwenthal's process as modified by Counciler and Schröder, and Procter (*v. Bull.* 13, Chem. Div. of U.S. Dept. of Agric. 890).

A simpler method, giving good results, is that of Tatlock and Thomson, based on the precipitation of the tannin with quinine and weighing as quinine tannate. Cinchonine might be used with advantage instead of quinine as in Chapman's method for the estimation of tannin in hops (*v. Analyst*, 1910, 104 ; *Smith, Analyst*, 1913, 312). In a series of analyses by the cinchonine method, Smith found amounts of tannin in Indian, Ceylon, and China teas varying from 11.6 to 16.9 p.c.

The recorded percentages of tannin vary greatly, mainly owing to the different methods of analysis employed. In normal teas the tannin should not be less than about 6 p.c., but may exceed 20 p.c. Wigner's analysis gave the following results in exceptionally astringent teas :—

	Tannin p.c.
Mayon Young Hyson tea . .	39.0
Very choice Assam	33.0
India Young Hyson	39.0
Assam (from Dr. McNamara's garden)	27.7
Caper, mixed	42.3

Tannin is present in all stages of development of the tea leaf, and in all qualities of tea ; the

tannin content is higher in the young leaves and in the best qualities of tea. Teas grown at the highest elevations are best and richest in tannin. During rolling both the acid content and the soluble tannin increase, but the latter decreases during fermentation by the agency of enzymes (Schulte im Hofe).

The presence of quercitrin in the fresh leaves of *Camellia theifera* and in dried tea may be shown as follows: An aqueous extract of the material is filtered, treated with 1-2 p.c. of concentrated hydrochloric acid and boiled for 1-2 hours, under a reflux condenser, whilst a rapid stream of carbon dioxide is passed through. A brownish precipitate is formed, which is thoroughly washed with water, dried at 100°C., and extracted with ether, when quercetin is removed and crystallised from boiling water. Since the leaves contain no quercetin this substance must have been formed by the hydrolysis of quercitrin in the leaves, and consequently its formation constitutes a proof of the presence of the latter substance. The amount of quercitrin present is about 0.1 p.c., and is the same whether the leaves have been grown in the shade

or exposed to sunlight (J. J. B. Deuss, Rec. trav. chim. 1923, 42, 623-624; J. Soc. Chem. Ind. 1923, 42, 904 A-905 A).

The amount of *ash* is fairly uniform in all teas, and varies from a little below 5 to rather more than 7 p.c. It is always rich in potash and phosphates, and manganese is such a constant constituent as to be almost characteristic. Zöller found the constituents to be as follows (Doc. du Lab. Municip. de Paris, 500) :—

	P.c.
Potash	39.22
Soda	0.65
Magnesia	6.47
Lime	4.24
Oxide of iron	4.38
Manganous oxide	1.03
Phosphoric acid	14.55
Sulphuric acid	trace
Chlorine	0.81
Silica	4.35
Carbonic acid	24.30

The following results were obtained in the Inland Revenue Laboratory (J. Bell) :—

	Congou (low)	Congou (fine)	Hyson	Souchong	Moning	Assam	Gun- powder (fine)
Total ash on dry tea	6.10	6.94	6.46	5.99	8.29	6.49	6.67
Sand	3.08	8.51	2.17	1.51	13.37	3.72	5.66
Silica	6.35	9.27	5.93	3.77	9.47	2.51	6.52
Chlorine	1.06	1.07	1.12	1.01	0.99	0.97	1.11
Potassium, to satisfy chlorine	1.16	1.17	1.23	1.11	1.09	1.07	1.22
Potash, K ₂ O	34.38	28.87	35.66	34.29	26.83	37.71	30.69
Soda, Na ₂ O	0.62	1.07	0.80	0.34	0.50	0.97	1.27
Ferrous oxide, FeO	2.82	0.84	1.12	1.68	2.23	0.57	1.43
Alumina, Al ₂ O ₃	5.55	3.42	2.73	4.19	4.52	1.54	2.70
Manganese oxide, Mn ₃ O ₄	1.68	1.37	1.93	1.59	1.49	2.11	1.92
Lime, CaO	8.82	8.74	9.54	8.98	9.04	8.58	8.19
Magnesia, MgO	2.12	4.87	4.65	3.19	2.42	6.48	6.52
Phosphoric anhydride, P ₂ O ₅	14.11	14.68	14.11	18.54	12.69	14.74	16.15
Sulphuric anhydride, SO ₃	6.52	6.54	6.34	6.38	5.39	5.83	6.68
Carbonic anhydride, CO ₂	11.73	9.58	12.67	13.42	9.97	13.20	9.94

A determination of the amount of ash alone may serve to detect the presence of leaves other than those of the tea plant, for these usually differ largely from tea leaves in the amount of their ash. The soluble ash in genuine tea is relatively high, usually exceeding half the amount of total ash, whilst foreign leaves likely to be used as an adulterant for tea generally contain a much smaller proportion of soluble ash than genuine tea. Paraguay tea, however, contains about the same amount of ash as true tea, but a larger proportion of soluble ash.

Almost the whole of the insoluble portion of the ash dissolves in hydrochloric acid; the insoluble residue is usually less than 1 p.c., any excess being due to sand or silicious matter.

The table, p. 717, gives the amount of ash in various teas dried at 100°, together with the proportion of ash soluble in water and insoluble in dilute mineral acids, and the alkalinity of the ash (Bell).

In tea leaves which have been infused in the ordinary way for domestic use, the amounts of

ash and other constituents shown in the next table were as follows :—

Description	Per- centage of ash	Percentage of ash			Alka- linity as K ₂ O
		Soluble in water	Soluble in dilute acids	In- soluble in acids	
Congou	3.92	0.54	2.97	0.41	0.11
Moning	4.53	0.85	2.73	0.95	0.28
Orange Pekoe	3.77	0.68	2.52	0.57	0.18
Hyson	5.56	0.76	3.40	1.40	0.21
Souchong	4.12	0.81	2.61	0.70	0.19
Average	4.38	0.73	2.85	0.81	0.19

Very little was known about the *essential oil* of tea prior to the researches of Van Romburgh in 1896, the chief results of which were as follows :—

440 lbs. of fresh leaves of tea distilled with water gave but *traces* of an essential oil, having a strong odour of tea. The water contained methyl

alcohol and a very volatile product giving aldehyde reactions (possibly it contains diacetyl).

From *rolled and fermented* fresh leaves, besides the products above mentioned, an essential oil was obtained in larger amount (3 c.c. from 100 lbs. of tea), or about 0.006 p.c.

The oil has a yellowish colour and a penetrating odour of tea; sp.gr. 0.866 at 26°. It rotates polarised light 0° 10' to the left in a 200 mm. tube. Fractional distillation separated it into two parts, the main portion boiling below

170° and the other above that temperature. The larger fraction consisted of a colourless liquid boiling from 153°–154° (bar. 740 mm.) with a strong odour of tea; sp.gr. 0.855 at 27°. Elementary analysis and the vapour density determinations indicated the formula $C_6H_{12}O$.

Sodium hydroxide and hydroxylamine have no action. With hydrochloric acid and acetic anhydride and with benzoylchloride and sodium hydroxide it gives esters. A solution of bromine in chloroform is decolorised with evolution of

Description	Percentage of		Percentage of ash			Alkalinity as K_2O
	Moisture	Ash	Soluble in water	Soluble in dilute acids	Insoluble in acids, sand	
Shanghai Congou, common . . .	9.07	7.63	3.23	3.02	1.38	1.40
" " " " . . .	9.22	5.95	3.55	2.12	0.28	1.55
" " fine . . .	8.51	7.41	4.02	2.54	0.85	1.76
" " " " . . .	8.56	6.62	3.72	2.25	0.65	1.50
" Moyune Young Hyson, common . . .	7.49	7.49	3.83	2.75	0.91	1.70
" " " " fine . . .	6.90	7.47	3.82	2.52	1.13	1.61
" " Hyson, common . . .	7.29	6.46	3.18	2.43	0.85	1.51
" " " " . . .	7.25	6.55	3.82	2.37	0.36	1.71
" " " " fine . . .	8.65	6.85	3.58	2.29	0.98	1.53
Foochow Congou siftings . . .	8.51	6.87	3.60	2.81	0.46	1.50
" " common . . .	9.35	7.34	3.37	2.97	1.00	1.55
" " fine . . .	9.09	6.89	4.01	2.32	0.56	1.77
" Scented Orange Pekoe, common . . .	7.55	7.17	3.56	2.86	0.75	1.69
" " " " fine . . .	7.70	6.72	3.99	2.27	0.46	1.60
" Souchong, common . . .	8.45	6.43	2.97	2.76	0.70	1.51
" " " " . . .	9.34	6.18	3.77	2.09	0.32	1.60
" " finest . . .	9.36	5.85	3.61	1.95	0.29	1.71
" Moning, common . . .	8.92	6.88	3.55	2.57	0.76	1.44
Canton Scented Caper, common . . .	6.87	6.38	3.21	2.49	0.68	1.50
" " " " fine . . .	6.63	6.63	3.47	2.23	0.93	1.46
" " Orange Pekoe, common . . .	7.02	6.63	3.72	2.33	0.58	1.67
" " " " fine . . .	7.73	7.09	4.10	2.46	0.53	1.92
" Gunpowder . . .	7.08	6.70	3.54	2.54	0.62	1.31
Indian, Kaugra Valley Young Hyson . . .	7.36	6.12	3.44	2.25	0.43	1.55
" Pekoe Souchong . . .	8.28	6.28	3.24	2.42	0.62	1.60
Himalaya Orange Pekoe . . .	7.84	7.62	3.45	2.83	1.34	1.63
Chittagong " " . . .	8.92	6.20	4.23	1.77	0.20	1.86
Assam Orange Pekoe . . .	9.41	5.93	3.78	1.93	0.22	1.63
" Pekoe Dust . . .	9.57	6.77	3.55	2.69	0.53	1.71
" " " " . . .	9.35	6.14	3.70	2.15	0.29	1.67
Darjeeling . . .	9.06	5.73	3.68	1.86	0.19	1.67
Chittagong Congou . . .	9.68	5.66	3.53	1.87	0.26	1.91
Average . . .	8.31	6.64	3.62	2.40	0.63	1.62

heat. It combines with 1 mol. of bromine. Treated with a neutral solution of potassium permanganate it is oxidised. All these reactions make it clear that the main portion of the oil consists of an unsaturated alcohol $\Delta\gamma$ -hexene- α -ol, $CH_2Et : CH \cdot CH_2 \cdot CH_2 \cdot OH$, identical with that obtained by Walbaum from Japanese oil of peppermint (Van Romburgh, Proc. K. Akad. Wetensch. Amsterdam, 1920, 22, 758).

The higher boiling portions of the oil contained about 1 p.c. of methyl salicylate (Van Romburgh).

A *non-drying oil*, somewhat resembling olive oil, is obtained from tea-seeds in China and Assam, the former yielding from 30 to 35 p.c. and the latter from 43 to 45 p.c. of oil. The first

pressings are used as an edible oil, although somewhat objectionable owing to the presence of saponin which is present to the extent of 7 or 8 p.c. in the resulting oil-cake. It is therefore unsuitable for feeding purposes, but has been recommended for use as a vermicide for dressing lawns. The lower qualities of oil are employed for illuminating, and for soap-making. Fine lubricating oils are also obtained from the seeds of other species of *Thea* in Japan.

The highest amount of *moisture* present in air-dried tea is 16 p.c. According to Wigner, the mean of the amounts yielded by driest Hysons and gunpowders and the moistest Congous is 7.67 p.c. Dragendorff found the average amount of moisture in twenty-three teas of

Russian commerce to be 10 p.c. Pélégot gives the amount in black tea as 10 p.c. ; in green tea as 8 p.c. Bell (see table above) found in 32 samples of tea of different kinds and from various sources that the proportion of moisture varied from 6.6 to 9.7 p.c., the average being 8.3 p.c.

Nitrogen is present in tea both in the form of caffeine and albuminous bodies, and to a greater extent than in most other leaves. Choline and xanthine bases have also been identified in tea.

Pélégot (Documents du Laboratoire Municipal de Paris, 501) gives the following percentages of total nitrogen :—

Gunpowder	6.62
Pekoe	6.28
Souchong	6.15
Assam	5.10

Gluten or legumen forms a quarter of the weight of the leaves according to Johnstone and Church (Chemistry of Common Life) ; but as it is hardly soluble in water, it is of no practical dietetic value. More will be dissolved if soda be added to the water. The ‘brick tea’ used in Thibet is boiled in the alkaline steppe-water which extracts the greater part of the gluten.

Tea infusion.—The amount of matter extracted by water from tea is capable of giving useful indications, but truly comparable results can be obtained only by rigid uniformity in the details of the extraction process. The methods are based on complete extraction and weighing either the extract or the insoluble portion ; or partial extraction by infusion and determination of the specific gravity of the infusion.

Pélégot (*vide supra*), using the first method, found the following percentages of total extractive on the dried leaves :—

Green teas.		Black teas.	
Gunpowder	. 51.9	Assam	. 45.4
Hyson	. 47.7	Bohea	. 44.4
„ skins	. 43.5	Congo	. 40.9
Young Hyson	. 51.5	Pekoe	. 34.6
Imperial	. 43.1	„ orange	. 48.7
Schoulang	. 45.9	Souchong (fine)	. 45.7
Tonkay	. 42.2	„ (ordinary)	. 41.8

Tatlock and Thomson (Analyst, 1910, 104) adopted the second method, finding the extract by difference ; and in order to avoid loss due to the solidification of extractive matter on cooling, they greatly increased the proportion of water, boiling 1 grm. of tea with 100 c.c. of water for 1 hour under a reflux condenser, filtering, washing with 80 c.c. of hot water, drying at 100° C. and weighing the insoluble residue on a tared filter. They found the following percentages of aqueous extract :—

	Variations	Average
Indian teas (10)	. . 43.5–49.7	46.4
Ceylon „ (5)	. . 41.3–48.2	44.1
China „ (6)	. . 38.4–46.9	43.1

O. Kellner, in conjunction with S. Ishii and M. Kamoshita, determined the proportions of the constituents of tea in the *infusions ordinarily drunk* in Japan. The methods of making the infusions are, however, different from those employed in this country. They are :

1. For Yenchá, extra-fine green tea, the

leaves are ground to powder, and drunk with the infusion.

2. For superior green tea the leaves are digested for 2 mins. with water at a temperature of 50°–60°C.

3. For medium green tea, boiling water is poured on the leaves, and stands on them for 1 minute.

4. For inferior tea, the leaves are boiled with water.

The object in all these methods is to extract as much caffeine and oil as possible, together with a moderate amount only of tannin.

Kellner digested 90 grms. superior green tea with half a litre of distilled water at 50° C. After 5 mins. the infusion was poured off, and another half-litre of water at 50° C. was added to the leaves. This was repeated three times, and each infusion was analysed separately.

The boiling-water method gives different results. Kellner digested 100 grms. of superior tea with 1 litre boiling distilled water, and the first infusion contained more than the sum of the contents of the three infusions by the warm-water method. The following table gives a summary of his results :—

PERCENTAGE AMOUNT OF EACH CONSTITUENT DISSOLVED.					
	Warm water			Total	Boiling water
	First infusion	Second infusion	Third infusion		
Dry matter	5.3	4.7	3.6	13.6	16.1
Caffeine	. 14.6	12.0	12.3	38.9	40.1
Tannin	. 15.9	14.4	13.9	44.2	36.8
Total nitrogen	5.2	4.7	4.4	14.3	17.1
Ash	. 17.1	14.4	4.9	36.4	36.1
Potash	. 15.1	15.1	6.1	36.3	43.3

In the following table, p. 719, by Tatlock and Thomson (Analyst, 1910, 108) are shown the percentage of the total extractive, caffeine, and tannin obtained in a 3-mins. and a 5-mins. infusion respectively. The columns are numbered to correspond with the teas of which the proximate analyses are given above (p. 714).

According to R. E. Andrew (J. Assoc. Off. Agric. Chemists, 1923, 7, 154) the following procedure has been favourably reported on by a number of analysts, and is recommended for adoption as the official method for estimating the water-extract in tea : 2 grms. of the ground sample are treated with 200 c.c. of hot water in a 500 c.c. measuring flask closed with a rubber stopper, through which passes a glass tube 30 inches long as condenser. The liquid is boiled gently, so that no steam escapes from the tube, for an hour, with occasional rotation of the flask. The cooled liquid is afterwards made up to volume, mixed, and filtered through a dry filter paper, 50 c.c. of the filtrate being evaporated to dryness over a steam-bath and the residue dried in an oven at 100°C. for an hour, cooled, and weighed (Analyst, 1924, 49, 141).

A strong decoction of tea frequently becomes turbid on cooling, and is covered with a thin pellicle caused by the separating out of caffeine tannate. The infusion also grows darker as it stands. This is probably due to the increase of

tannin in solution and its alteration by oxidation.

With regard to infusions of tea, it should be remembered that different results are obtained from the same tea, according to whether the water used is hard or soft. The larger wholesale dealers have analyses made of the waters used in the different towns and districts which they supply, and blend different teas so as to suit the requirements of different neighbourhoods, the blend depending on the particular water used in each.

In judging the *commercial value* of tea the professional tea-taster makes an infusion by pouring about 100 c.c. of boiling water upon 3 grms. of tea, allowing to infuse for 5 mins. and then decanting the liquor. He is guided mainly by the colour, uniformity, and age of the leaf, and by the bouquet, flavour, and pungency of the infusion. These are usually supposed to depend upon the amount and quality of the volatile oil, but there is good reason to believe that they are intimately associated with the action of certain enzymes in the leaf.

Although considerations other than chemical composition affect the commercial value of tea, as the age, size, and condition of the leaf, whether whole, broken, tea-dust, or fannings, yet in teas accepted by expert tea-tasters as of fine quality, a certain uniformity has been observed in the ratio of the caffeine to the tannin. This is as one to three, indicating a *compound* of caffeine and tannin already referred to as caffeine tannate (*see Lancet, Jan. 1911*).

In this form the special characteristics of both caffeine and tannin in the free state are neutralised in the compound, which differs in chemical and physiological properties from, and has none of the objectionable qualities of either of its constituents. In inferior or common teas either caffeine or tannin is present in excess of this ratio, the former imparting a bitter taste to the infusion, and the latter increasing its astringency. The proper balance may be attained by suitable blending.

Adulteration in its old forms is very little practised now, probably not at all in this country. Inferior teas from old stocks are sometimes sold, also teas recovered from wrecked

RESULTS OF INFUSION PER 100 PARTS OF INGREDIENTS EXTRACTED.

—	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22
<i>Three Minutes' Infusion.</i>																						
Water extract	74	60	83	60	72	—	67	66	75	65	72	71	60	67	72	61	54	55	63	60	60	75
Caffeine. .	76	55	59	39	73	—	46	50	73	51	69	60	41	67	69	72	66	54	73	73	68	68
Tannin. .	61	46	70	41	57	—	58	56	57	50	52	60	42	58	59	49	39	41	46	41	49	42
<i>Five Minutes' Infusion</i>																						
Water extract	88	73	90	70	83	—	79	79	83	72	89	85	76	85	89	75	65	67	71	78	77	81
Caffeine. .	87	61	82	52	82	—	65	71	82	70	80	74	69	86	80	86	83	85	84	85	83	81
Tannin. .	79	73	86	50	70	—	67	69	70	62	74	74	67	67	74	62	60	60	61	64	63	60

vessels and re-dried, but owing to the examination by the Customs Authorities (acting under the Sale of Food and Drugs Act, 1875) of all tea imported into the United Kingdom, and the general soundness of the tea trade, the importation of adulterated tea is practically a thing of the past.

The modes of adulteration formerly common were :—

1. Adding leaves of different kinds, the principal being ash, beech, birch, bramble, camellia, chestnut, coffee, currant, elder, elm, gooseberry, hawthorn, plum, poplar, raspberry, and willow.

2. Adding 'exhausted' leaves, *i.e.* tea leaves that had already been used.

3. 'Facing' black tea with graphite and adding colouring matters to green tea, notably indigo, Prussian-blue, turmeric, mixed with China clay, soapstone, &c. Copper salts are scarcely ever employed, but occasionally a little iron sulphate is used to impart astringency to the tea. The facing material rarely amounts to 1 p.e., and is usually free from deleterious ingredients, being for the most part insoluble in water. For a method of estimating Prussian-blue in tea, *see Knight, J. Ind. Eng. Chem.* 1914, 6, 909.

4. Adding catechu and other astringent principles.

5. Adding sand containing ferric oxide to increase the weight of the tea.

Foreign leaves are detected by the microscope. Drawings of leaves principally used as tea adulterants will be found in Bell's Foods, in Bulletin No. 13, U.S. Dept. of Agriculture, and in Villiers and Collin's *Traité des Altérations et Falsifications des Substances Alimentaires*.

Indications as to the presence of exhausted leaves may be obtained by determinations of the caffeine, tannin, and in particular by the alkalinity of the ash and the proportion of it soluble in water.

The substances used for 'facing' tea can generally be readily removed for examination by shaking up with cold water, pouring off the liquor, and allowing the matter in suspension to subside.

An imitation tea known as 'lie tea' was formerly made in China from the sweepings of the tea-warehouses, foreign leaves, and mineral matter, coloured by one of the 'facing' preparations, cemented together by rice starch and rolled into grains. The percentage of ash in 'lie tea' was always high, often exceeding 50 p.c.

Brick tea. This variety of tea is used largely in Thibet, Western Siberia, and Russia. The cheaper and inferior kinds are very coarse, consisting of both leaves and twigs, frequently mixed with a glutinous rice paste to make them cohere, and compressed by hand into blocks. The curing of the leaf consists simply of a few minutes' heating in iron pans, a slight fermentation by storing in heaps in the 'hongs' or factories, then drying in the sun, sorting into grades, and steaming preparatory to pressure in shallow moulds of the required shape and size in which the blocks are left for 3 or 4 days to harden. Over twenty million pounds of this kind of tea are said to be consumed annually in Thibet.

A superior kind of brick tea is made, chiefly at Hankow, from tea-dust which, after sifting and grading, is steamed and compressed in moulds into bricks or cakes by means of an hydraulic press, the blocks being left in the moulds for 2 or 3 weeks until thoroughly dry and hard.

Nearly fifty million pounds of this tea are made annually, chiefly for the Russian Government, in factories under Russian control, and large quantities of Indian tea-dust are utilised in the manufacture of this variety of brick tea. The finest grades are made in 'tablet' form, mainly for consumption in European Russia.

Amongst certain Himalayan tribes in Thibet, and in Western Siberia, it is a common practice to eat the tea residue, after the infusion has been drunk, mixed with sugar, milk, butter, or other fat. It is very nutritious and forms the food of the natives for weeks at a time.

Different plants are used as tea in different parts of the world. The chief of these is the *Ilex paraguayensis*, or Brazilian holly, the leaves of which make what is known as Paraguay tea or 'maté' (q.v.).

Other plants whose leaves are used to make tea are:—

Angræcum fragrans (Thou.) (an orchid) makes the 'Faham tea' of Mauritius.

Catha edulis (Forsk.) makes 'Abyssinian tea,' known as 'Kât' or 'Kaat.'

Coffee-tree (*Coffea arabica* [Linn.]).

Cyclopia subternata (Vog.) ('Boer Tea,' 'Cape tea,' or 'Bush tea').

Glaphyria nitida (Jack) (a species of myrtle), in the Eastern Archipelago.

Ledum palustre (Linn.) and *Ledum latifolium* (Jacq.) make 'Labrador tea.'

Lithospermum officinale (Linn.), 'Gromwell' or 'Bohemian tea.'

Various species of *Melaleuca* and *Leptospermum* (belonging to the myrtle order), various species of *Correa* (belonging to the *Rutaceæ*); *Acæna Sanguisorbæ* (Vohl.) (allied to the *Rosaceæ*), and the bark of the Australian *Sassafras*, make the 'Abyssinian tea' of Australia and Tasmania.

All the above teas, except Bohemian tea, Bush tea, and Faham tea, contain caffeine, and all have a volatile oil, and an astringent principle allied to tannin. J. C.

TEALLITE. A sulphostannite of lead, $PbSnS_2$ (Sn 30.5 p.c.), crystallised in the orthorhombic system. The thin, graphite-like folia are nearly square in outline and have a perfect cleavage parallel to their large surface. The

colour is greyish-black with metallic lustre. Sp.gr. 6.36; hardness 1–2. It is of rare occurrence in Bolivia, perhaps from the same localities as the related tin-ores cylindrite and franckeite (q.v.) (G. T. Prior, Min. Mag. 1904, 14, 21). L. J. S.

TEA SEED OIL is the expressed oil of the seeds of *Camellia theifera*. It is a clear straw or amber-coloured yellow oil, resembling olive oil, but without smell or taste. The expressed oil frequently contains a poisonous saponin which renders it unfit for edible purposes. The oil obtained by extraction with solvents is free from saponin (Weit, Arch. d. Pharm. 239, 365).

Other varieties of the oil are the Chinese or sasanqua oil, the expressed oil of the seeds of *Thea sasanqua*, Assam oil, and Japanese or Tsabaki oil, the expressed oil of the seeds of *Thea Japonica*. They have very similar physical constants as under:

Specific gravity . . .	0.9028–0.9188
Saponification value . .	180.9–192.6
Iodine number . . .	80.1–92.7
Reichert-Meissl value . .	1.17–0.5
Refractive index at 20° .	1.4679–1.4707

Tea seed oil is occasionally used to adulterate olive oil.

TELÆSCIN v. HORSE-CHESTNUT.

TELLURITE v. TELLURIUM.

TELLURIUM. Sym. Te. At.wt. 127.5 (Stahler and Tesch); 127.7 (Bruylants and Desmat); 127.8 (Bruylants and Michielsen).

The presence of a new metal was suspected in an auriferous mineral from Transylvania by Müller von Reichenstein in 1782; from this mineral tellurium was isolated by Kitaibel in 1789, and its existence confirmed by Klaproth in 1798, who gave it its name (Crell's Ann. 1798, 91). The element was more fully studied by Berzelius (Pogg. Ann. 1826, 8, 411; 1833, 28, 392; 1834, 32, 1, 577). See also Diergart (Zeitsch. angew. Chem. 1920, 33, 299; Chem. Soc. Abstr. 1921, ii. 421).

For researches on tellurium of a general character, v. Brauner (Monatsh. 1889, 10, 416), Staudenmaier (Zeitsch. anorg. Chem. 1895, 10, 189), Retgers (*ibid.* 1896, 12, 98), Gutbier (*ibid.* 1902, 32, 51, 54), Metzner (Ann. Chim. 1898, [vii.] 15, 203).

Occurrence.—Tellurium occurs native in small quantity, associated with silver and gold; but it is usually found combined with metals as tellurides, the most important being *tetradymite* (Bi_2Te_3), *altäite* ($PbTe$), *coloradolite* ($HgTe$), *calaverite* ($AuTe_2$), *sylvanite* ($AuAgTe_4$), *petzite* (Ag_3AuTe_2), *nagyagite* ($(AuPb)_2(TeSSb)_3$). The chief localities are *Transylvania* (Petz, Pogg. Ann. 1842, 57, 467; Schönbein, Annalen, 1852, 86, 201; Loczka, Zeitsch. Kryst. 1892, 20, 317, 320; Muthmann and Schröder, *ibid.* 1897, 29, 140); *Colorado* (v. Chem. Soc. Abstr. 1896, 70, ii. 612, 613; 1898, 74, ii. 385; Amer. J. Sci. 1897, [iv.] 4, 306; 1898, [iv.] 5, 375, 377, 421, 428; 1900, [iv.] 10, 419, 427; 1904, [iv.] 18, 433; Bull. U.S. Geol. Survey, 1905, No. 262, 55); *West Australia* (v. Chem. Soc. Abstr. 1898, 74, ii. 385; Chem. News, 1900, 82, 272; Min. Mag. 1903, 13, 268; Eng. & Min. J. 1903, 75, 814; Ann. Mines, 1901, 19, 530); also *Mexico*, *Chile*, *Brazil*, *Honduras*, and *Asia*

Minor (v. Bull. Soc. chim. 1873, 20, 481; Bull. Acad. roy. Belg. 1908, 255).

Tellurite (TeO_2) or *tellurium ochre* also occurs, and 17 p.c. of tellurium has been found in the *red sulphur* of Japan (Divers and Shimidzu, Chem. News, 1883, 48, 284).

Preparation.—Tellurium is obtained from the preceding minerals or from the residues obtained in several metallurgical processes. Bismuth telluride, finely powdered, is mixed with sodium carbonate, rubbed up with oil to a thick paste, and calcined in a closed crucible. After lixiviating with cold water, a current of air is drawn through the aqueous solution of sodium telluride, when tellurium separates as a grey powder. Other tellurides are attacked with hydrochloric acid, the insoluble residue heated with concentrated sulphuric acid, and from the diluted sulphate solution, after removing silver as the chloride, the tellurium is precipitated by means of zinc or sulphur dioxide. For details and other methods, v. Berzelius, *l.c.*; Löwe, J. pr. Chem. 1853, 60, 163; Oppenheim, *ibid.* 1860, 81, 308; Farbaky, Zeitsch. angew. Chem. 1897, 10, 11.

The method of reduction of potassium anhydrotellurate by zinc and hydrochloric acid with the precipitation of metallic tellurium (*cf.* Chem. Soc. Abstr. 1920, ii. 174) is modified by using aluminium and sodium or potassium hydroxide for the production of nascent hydrogen, with the result that the reduction is completed in one hour instead of ten. The aluminium must be pure and free from copper (Hulot, Bull. Soc. chim. 1921, [iv.] 29, 1070; Chem. Soc. Abstr. 1922, ii. 142).

The alkaline residues from bismuth ores are acidified with hydrochloric acid and treated with sodium sulphide in order to precipitate the tellurium (Matthey, Proc. Roy. Soc. 1901, 68, 161). Tellurium is also extracted from the anode slimes obtained in the course of refining American copper by electrolysis (Whitehead, J. Amer. Chem. Soc. 1895, 17, 849, 855; Lenher, *ibid.* 1899, 21, 347, 351; Merriss and Binder, Eng. and Min. J. 1918, 106, 443).

The button of the noble metals obtained by cupellation of the slimes with lead is fused with sodium carbonate and nitrate, and the 'nitre slag' is extracted with hot water. On adding sulphuric acid a precipitate of tellurous acid is obtained. The dried tellurous acid is reduced with lampblack or ground charcoal in a crucible furnace and cast into cake or stick form. Or the tellurous acid may be dissolved in strong hydrochloric acid and the solution diluted and mixed with sulphur dioxide to precipitate tellurium.

Crude tellurium may be purified by boiling it with sodium sulphide solution and sulphur; from the filtered liquid pure tellurium is precipitated by heating with sodium sulphite (Schelle, 7th Inter. Cong. Appl. Chem. 1909, sect. III. A. 80). For its complete purification, the element is dissolved in *aqua regia*, evaporated several times with hydrochloric acid, and precipitated by sulphur dioxide from the diluted and filtered chloride solution. The precipitate is fused with potassium cyanide in a current of coal gas, the mass extracted with water, filtered, and the tellurium precipitated by aspirating air through the solution. The element is converted into telluric acid by Staudenmaier's method (v.

infra), purified by several recrystallisations, ignited to tellurium dioxide, and the latter dissolved in hydrochloric acid. The pure element, precipitated by sulphur dioxide or hydrazine from the chloride solution, is dried and distilled in a current of hydrogen (Brauner, Monatsh. 1889, 10, 416; Chem. Soc. Trans. 1889, 55, 382; Baker and Bennett, *ibid.* 1907, 91, 1849).

Properties.—Tellurium is a silver-white, lustrous, brittle, metallic-looking substance, which crystallises in hexagonal rhombohedra isomorphous with sulphur and selenium (Muthmann, Zeitsch. physikal. Chem. 1891, 8, 396). It exists in two forms, Te_α and Te_β , which are present as dynamic allotropes in equilibrium, $\text{Te}_\alpha \rightleftharpoons \text{Te}_\beta$. The equilibrium amounts are changed by alteration in temperature. The treatment to which tellurium is subjected influences the density in a marked degree; it varies between 6.272 and 5.949, depending on the temperature (Cohen and Kröner, Zeitsch. physikal. Chem. 1913, 82, 587; but see *infra*). It melts at 452° , boils at a red heat, and volatilises readily when heated in a stream of hydrogen. In an almost perfect vacuum it boils at 478° (Krafft, Ber. 1903, 36, 4344). The vapour of tellurium is pale yellow at low temperatures, becomes deep red at 1250° , and again pale yellow at 1350° , when it consists of diatomic molecules (Deville and Troost, Compt. rend. 1863, 56, 891; Biltz, Zeitsch. physikal. Chem. 1894, 19, 415; Dobbie and Fox, Proc. Roy. Soc. 1920, 147).

For the hardness and microstructure of tellurium compounds, see Saldau (Chem. Soc. Abstr. 1915, ii. 683).

Pharmacology.—The ions of tellurous and selenious acids are much more active than those of telluric and selenic acids. The growth of moulds is scarcely affected by the action of tellurites and tellurates. Bacteria, especially of the typhus-coli group, are, on the other hand, very sensitive to the action of these substances. For the action of tellurium salts on bacteria, see Joachimoglu (Chem. Soc. Abstr. 1922, i. 1095). Joachimoglu (Biochem. Zeitsch. 1920, 107, 300) suggests the application of tellurium compounds in the chemotherapy of typhoid infection (Chem. Soc. Abstr. 1920, i. 793). See also Joachimoglu and Hirose (Chem. Soc. Abstr. 1922, i. 396; i. 406).

Turina (Biochem. Zeitsch. 1922, 129, 507) has examined the action of selenites, selenates, sulphites, sulphates, tellurites, and tellurates on the germination of plants and on the mature plant. From the deposition of selenium and tellurium by reduction in the tissues, it is concluded that neither selenium nor tellurium salts enter the system in appreciable quantities by way of the root hairs, but that the root-cap plays the important role of point of entry and filtration for nutritive salts (Chem. Soc. Abstr. 1922, i. 707).

For the bactericidal action of tellurium β -di-ketones, see Morgan, Cooper and Corby (J. Soc. Chem. Ind. 1924, 43, 304 T).

Tellurium is precipitated by reducing agents in an amorphous form, sp.gr. 6.015. When heated, it is converted into the crystalline form with evolution of heat (Fabre and Berthelot, Compt. rend. 104, 1405).

Allotropy of tellurium.—Density determinations made by Damiens (Compt. rend. 1922, 174, 1344) on tellurium carefully purified by distillation in hydrogen and then in a vacuum, the material being subsequently crystallised either by vaporisation or by slow cooling of the molten material, do not confirm the views of Cohen and Kröner (Zeitsch. physikal. Chem. 1913, 82, 587) as to the dynamic allotropy of tellurium. Tellurium obtained by vaporisation has d 6.310, and is not changed by long heating at various temperatures. Specimens prepared in other ways show a slightly lower density, as, owing to the manner of preparation, they are slightly porous. Amorphous tellurium has d 5.85–5.87; on heating, it is transformed into crystalline tellurium with development of heat and its density rises (Chem. Soc. Abstr. 1922, ii. 498).

For a summary of literature on allotropy of tellurium, *v.* Cohen and Kröner (Chem. Weekblad. 1910, 7, 57).

From a study of the heats of reaction of different forms of tellurium with a mixture of bromine and bromine water, Berthelot and Fabre have found the following relationship holds: $\text{Te}_{\text{cryst.}} = \text{Te}_{\text{amorp.}} + 12.096$ cal. (for 64 grms.). Previous work on the allotropy of tellurium did not confirm this equation (*cf.* Chem. Soc. Abstr. 1922, ii. 498), and A. Damiens (Compt. rend. 1922, 174, 1548) has accordingly repeated the work of Berthelot and Fabre, using, however, a mixture of bromine and concentrated hydrochloric acid diluted with its own volume of water. His results do not confirm those of Berthelot and Fabre, but establish the equation $\text{Te}_{\text{amorp.}} = \text{Te}_{\text{cryst.}} + 2.63$ cal., which is in accord with his work on the allotropy of tellurium (*l.c.*) (Chem. Soc. Abstr. 1922, ii. 562).

By careful reduction in dilute solution, brown and blue colloidal solutions of tellurium can be prepared (Gutbier, Zeitsch. anorg. Chem. 1902, 32, 51, 91; 1904, 40, 264; 42, 177; Paal and Koch, Ber. 1905, 38, 534; Weimarn and Maljischeff, J. Russ. Phys. Chem. Soc. 1910, 42, 484).

For the action of sodium hyposulphite on tellurium, *see* Tschugaev and Chlopin (Ber. 1914, 47, 1269; Chem. Soc. Abstr. 1915, ii. 554).

Tellurium shows a marked fluorescence in the gaseous condition in the most refrangible part of the visible region. The spectrum is discontinuous and shows more or less feeble groups of lines which have the appearance of bands (Steubing, Zeitsch. physikal. Chem. 1913, 14, 887; Diestelmeier, Zeitsch. wiss. Photochem. 1915, 15, 18).

For the emission spectrum of tellurium, *v.* Salet, Compt. rend. 1871, 73, 559, 742; Ann. Chim. 1873, 28, 49; Ditte, Compt. rend. 1871, 73, 262; Hartley, Chem. Soc. Trans. 1883, 43, 399; de Grammont, Compt. rend. 1898, 127, 866, 868; for spark spectrum, *v.* Watts, Spectrum Analysis, p. 28; and for absorption spectrum, *v.* Gernez, Compt. rend. 1872, 74, 1190. *See also* Lindsay, Compt. rend. 1922, 175, 150; Chem. Soc. Abstr. 1922, ii. 599. For arc spectrum, *v.* Uhler and Patterson, Amer. J. Sci. 1913, [iv.] 36, 135. For the high frequency spectrum, *see* Siegbahn, Chem. Soc. Abstr. 1916, ii. 462.

Tellurium burns in air with a blue flame, forming the dioxide. It is not attacked by hydrochloric acid, but reacts with nitric or sulphuric acid, and also with concentrated potassium hydroxide. It is very slowly attacked by hydrogen peroxide. It is insoluble in carbon disulphide. For the solution of tellurium in absolute sulphuric acid, *see* E. Moles (Chem. Soc. Abstr. 1915, ii. 335). Tellurium reduces solutions of gold and silver salts (Hall and Lenher, J. Amer. Chem. Soc. 1902, 24, 918) and reacts with thionyl chloride and similar chlorides (Lenher and Hill, *ibid.* 1908, 30, 737; Horváth, Zeitsch. anorg. Chem. 1911, 70, 408; Prandtl and Borinski, *ibid.* 1909, 62, 237), the tetrachloride being usually obtained. For its behaviour as an electrode, *v.* Le Blanc, Zeitsch. Elektrochem. 1905, 11, 521, 813, 931; 1906, 12, 649. In physical properties tellurium resembles the metals, but chemically it is decidedly non-metallic. It forms one of the oxygen family of elements and closely resembles sulphur and selenium. This is shown by the fact that the three elements are isomorphous, and form mixed crystals when crystallising either from solution in a solvent or from the fused mixture (*v. infra*). The compounds $\text{Te}(\text{C}_6\text{H}_5)_2\text{Br}_2$ and $\text{Se}(\text{C}_6\text{H}_5)_2\text{Br}_2$ are isomorphous, as also are selenium and tellurium dimethylamine bromides and chlorides; whilst the acid selenates and tellurates of rubidium have been shown to form mixed crystals (Muthmann, Zeitsch. physikal. Chem. 1891, 8, 396; Norris and Mummers, Amer. Chem. J. 1900, 23, 486; Pellini, Atti R. Accad. Lincei, 1906, 15, i. 629, 711; 15, ii. 46; 1909, 18, i. 701; 18, ii. 19, 279).

For the magnetic susceptibility of tellurium, *see* Wistrand (Chem. Soc. Abstr. 1920, ii. 527).

For the equilibrium of aluminium and tellurium, *see* Chikashige and Nosé (Mem. Coll. Sci. Kyoto, 1917, 2, 227; Chem. Soc. Abstr. 1918, ii. 114). The equilibrium in the system iodine and tellurium, *see* Damiens (Compt. rend. 1920, 171, 1140; Chem. Soc. Abstr. 1921, ii. 110, 257). Equilibrium of mixtures of sodium and tellurium in liquid ammonia, *see* Kraus and Chin (Chem. Soc. Abstr. 1922, ii. 765).

If elementary tellurium is added to an ordinary lime soda glass and fused under reducing conditions, glasses are obtained of colours varying with the amount and condition of the element, some containing colloidal solutions, others polytellurides. The former correspond with the tellurium hydrosols and are blue or brown, depending upon the size of the particles, the blue glass containing the larger particles. The glass containing polytellurides is red, or violet-red, and has an absorption spectrum identical with that of aqueous solutions of polytellurides (Fenaroli, Chem. Zeit. 1914, 38, 873; Kolloid Zeitsch. 1915, 16, 53).

Atomic weight.—This is of particular interest, since, judging by the well-defined chemical similarities exhibited by sulphur, selenium, and tellurium, the atomic weight of tellurium would be expected to be less than that of iodine, in order that tellurium and iodine might fit into the Periodic Classification in the places that would be assigned to them from a consideration of their chemical properties. The atomic weight of tellurium is, however, found to be 127.5,

distinctly higher than that of iodine (126.9). According to Kusnetzov (Chem. Zentr. 1913, i. 772; Chem. Soc. Abstr. 1913, ii. 403), when the differences between the atomic weights of the elements in the uneven periods are tabulated, they show a regular rise and fall within the separate groups. The negative difference between iodine and tellurium is in accordance with the other differences in the sixth group.

The anomaly in the atomic weight of tellurium might be assumed to be due to the want of homogeneity in what is known as tellurium, but the attempts made (Brauner, Monatsh. 1889, 10, 411; Chem. Soc. Trans. 1889, 55, 382; Baker and Bennett, *ibid.* 1907, 91, 1849; Baker, Chem. News, 1908, 97, 209; Staudenmaier, Zeitsch. anorg. Chem. 1895, 10, 189; Pellini, Gazz. chim. ital. 1902, 32, 131; Gutbier, Sitzungsber. phys.-med. Soc. Erlangen, 1906, 37, 270; Norris, J. Amer. Chem. Soc. 1906, 28, 1675; Lenher, *ibid.* 1908, 30, 741; 1909, 31, 20; Marckwald, Ber. 1907, 40, 4730; 1910, 43, 1710) to show that tellurium is not homogeneous and to disprove the individuality of what is known as the element tellurium have hitherto failed and the anomaly still remains to be satisfactorily accounted for; the positive results of Browning and Flint (Amer. J. Sci. 1909, 28, 347; 1910, 30, 209; J. Amer. Chem. Soc. 1912, 34, 1325; Chem. Soc. Abstr. 1912, ii. 1051) have not been confirmed by Harcourt and Baker (Chem. Soc. Trans. 1911, 99, 1311), or by Pellini (Atti R. Accad. Lincei, 1912, [v.] 21, i. 218), Dudley and Bowers (J. Amer. Chem. Soc. 1913, 35, 875), Stäpler and Tesch (Zeitsch. anorg. Chem. 1916, 98, 1). Flint (Chem. Soc. Abstr. 1910, ii. 845; 1912, ii. 1051) stated that by fractional hydrolysis of tellurium tetrachloride he obtained two fractions, one giving the atomic weight 124.3, and the other, which was still impure, the atomic weight 128.85. This work has been repeated with a larger quantity of material, but the results do not show progressive diminution of the atomic weight, and thus fail to confirm Flint's conclusion. In view of these experiments and those of other investigators, Morgan (J. Amer. Chem. Soc. 1912, 34, 1660) considers that the evidence for the homogeneity of tellurium is quite convincing (Chem. Soc. Abstr. 1913, ii. 41).

In Harcourt and Baker's discussion (Chem. Soc. Trans. 1911, 99, 1311) of the work of Browning and Flint on the hydrolysis of tellurous chloride, they state that the yellow colour sometimes observed in the hydrolytic fractions was found by them to be due to a small amount of telluric oxide present in their material, presumably because of chlorine set free from the hydrochloric acid by the action of bright sunlight. Browning and Oberhelman (Eighth Inter. Cong. App. Chem. 1912, 2, 59) find that if pure tellurous oxide is dissolved in hydrochloric acid which has been exposed to bright sunlight, the solution hydrolysed with boiling water, and the precipitate thus formed boiled with pure hydrochloric acid, no chlorine is liberated. Moreover, if the solution of tellurous oxide in hydrochloric acid is saturated with chlorine both before and after hydrolysis, the amount of chlorine liberated when the precipitate is boiled with hydrochloric acid is very

small, the amount of tellurium trioxide formed being less than 0.5 p.c.

It follows that the results obtained by Browning and Flint cannot be due to an error caused in the way suggested by Harcourt and Baker (Chem. Soc. Abstr. 1913, ii. 696).

The atomic weight has been determined on material prepared from widely different sources, by the syntheses and analyses of the dioxide and tetrabromide, by the analyses of telluric acid, the double bromide of tellurium and potassium, the basic nitrate, hydrogen telluride and other compounds, and by the measurement of its electro-chemical equivalent; the results point definitely to the value 127.5 as correct (*v.* the investigations cited above). The work described in this paper by Dennis and Anderson (J. Amer. Chem. Soc. 1914, 36, 882; Chem. Soc. Abstr. 1914, ii. 456) was undertaken in order to determine the atomic weight of tellurium and obtain evidence with regard to its alleged complexity. Magnesium and aluminium tellurides were prepared and hydrogen telluride was obtained by decomposing the latter compound with hydrochloric acid. The hydrogen telluride thus prepared was fractionally distilled, and the atomic weight of tellurium in the fractions was determined by means of the ratio $\text{Te}:\text{TeO}_2$. As this method of preparing hydrogen telluride was not altogether satisfactory a further quantity was obtained by electrolysis, using a tellurium cathode, a platinum anode, and a 50 p.c. solution of phosphoric acid as the electrolyte. The product was fractionally distilled, the twenty-one fractions were decomposed by passing the gas into nitric acid, and the solutions of tellurium dioxide and nitric acid thus obtained were evaporated to dryness and the residues fused. The atomic weight of the tellurium in the various fractions was determined by titrating the resulting tellurium dioxide with potassium permanganate. The results support the view that tellurium is not complex, and that the atomic weight 127.5 now assigned to it is the correct value. And *see also* Wills, Chem. Soc. Trans. 1879, 35, 704; Chikashigé, *ibid.* 1896, 69, 881; Gooch and Howland, Amer. J. Sci. 1894, 58, 375; Metzner, Compt. rend. 1898, 126, 1716; Koethner, Annalen, 1901, 319, 1; Scott, Chem. Soc. Proc. 1902, 18, 112; Gallo, Atti R. Accad. Lincei, 1905, [v.] 14, i. 23, 104; Bruylants and Desmet, Bull. Soc. chim. Belg. 1914, 28, 264. A spectrographic study of tellurium purified by fractional precipitation with hydrazine hydrochloride and separated into twenty fractions, showed no variations in their spectra, or indication of any breaking down or separation into parts differing in properties (Dudley and Jones, J. Amer. Chem. Soc. 1912, 34, 995; Dudley and Bowers, *ibid.* 1913, 35, 875). The lower value obtained by Steiner (Ber. 1901, 34, 570) by the combustion of tellurium diphenyl has not been confirmed; and it still remains to be discovered why the positions of tellurium and iodine in the Periodic Classification, determined by their atomic weights, should be the reverse of those which their chemical properties indicate.

It is, however, to be remarked (*v. supra*) that when the differences between the atomic weights of the elements in the uneven periods are

tabulated, they show a regular rise and fall within the separate groups. The negative difference between iodine and tellurium is in accordance with the other differences in the sixth group (Kusnetzov, Chem. Zentr. 1913, i. 772).

Tellurium reacts with iodine, and the cryoscopic and ebullioscopic results indicate a large proportion of single atoms (Beckmann and Hanslian, Zeitsch. anorg. Chem. 1912, 80, 221; Chem. Soc. Abstr. 1913, ii. 402).

Tellurides. A number of these compounds occur as minerals (*v. supra*). The following have been shown to exist by the methods of thermal and microscopic analysis, the mercury compound alone having no melting-point: AuTe_2 , Cu_4Te_3 , Cu_2Te , HgTe , CdTe , Tl_2Te , Tl_5Te_3 , Tl_2Te_5 , PbTe , SnTe , Sb_2Te_3 , As_2Te_3 , Bi_2Te_3 (Pélabon, Compt. rend. 1906, 142, 207; 1907, 145, 118; 1909, 148, 1176; Fay and Ashley, Amer. Chem. J. 1902, 27, 95; Fay and Gillson, *ibid.* 27, 81; Fay, J. Amer. Chem. Soc. 1907, 29, 1265; Pellini and Aureggi, Atti R. Accad. Lincei, 1909, 18, ii. 211; Pellini and Quercigh, *ibid.* 1910, 19, ii. 445; Pellini, Gazz. chim. ital. 1915, 45, i. 469; Chikashigé, Zeitsch. anorg. Chem. 1907, 54, 50; Biltz and Meklenburg, *ibid.* 1909, 64, 226; Kobayashi, *ibid.* 1910, 69, 1). By direct union of the elements K_2Te , Na_2Te , K_3Te_2 and TlTe can be obtained; numerous metallic tellurides have been prepared from aqueous solutions of these compounds by double decomposition; they are usually readily oxidised by air when moist (Tibbals, J. Amer. Chem. Soc. 1909, 31, 902). Carbon telluride CTe_2 is also known (Stock and Blumenthal, Ber. 1911, 44, 1832).

Hydrogen telluride TeH_2 , discovered by Davy (1810), is formed by the direct union of its elements, or by the action of dilute acids on the tellurides of zinc, aluminium, and magnesium. It is prepared by electrolysis of 50 p.c. sulphuric acid at -15°C ., using a piece of tellurium as cathode; the gas evolved at the cathode, when quickly dried, is nearly pure hydrogen telluride. The substance is a foetid-smelling, inflammable, extremely unstable gas, which condenses to a pale yellow liquid boiling at 0°C ., m.p. -57° . It has a vapour density of 65 ($\text{H}=1$) and contains its own volume of hydrogen. It resembles hydrogen sulphide in chemical properties and slowly undergoes dissociation. Its properties have been studied by Bruylants (Bull. Acad. roy. Belg. 1920, [v.] 6, 472). The triple point has for co-ordinates $t-45.4^\circ$, p 102 mm. The density d_0 2.65; b.p. at 760 mm. -1.8° . Latent heat of vaporisation (calc.) 45.7 cal. The critical temperature *circa* 200° (Ernyei, Zeitsch. anorg. Chem. 1900, 25, 313; Moser and Ertl, Zeitsch. anorg. Chem. 1921, 118, 269).

Solid hydrogen telluride forms white crystals, and melts at -57° to a very pale yellow liquid. Liquid hydrogen telluride boils at 0° , and when freshly distilled is almost colourless; when left, however, the colour gradually becomes darker, owing to the presence of dissolved tellurium formed by decomposition. When hydrogen telluride is left in sealed tubes, it slowly dissociates, tellurium being deposited on the walls; this change seems to take place as rapidly in the dark as in the light (Dennis and Anderson, J. Amer. Chem. Soc. 1914, 36, 882; Chem. Soc. Abstr. 1914, ii. 456).

COMPOUNDS WITH HALOGENS.

Tellurihalides, see Gutbier, Flury and Weinzierl (Zeitsch. anorg. Chem. 1914, 86, 169; Chem. Soc. Abstr. 1914, i. 502).

Tellurium tetrafluoride TeF_4 is formed when the dioxide is heated with hydrofluoric acid in a platinum retort; it distils over and forms a colourless, very deliquescent mass. The hydrate $\text{TeF}_4 \cdot 4\text{H}_2\text{O}$ separates from solutions in hydrofluoric acid. Numerous double fluorides, *e.g.* $\text{KF} \cdot \text{TeF}_4$, $\text{BaF}_2 \cdot 2\text{TeF}_4 \cdot \text{H}_2\text{O}$ are known (Metzner, Compt. rend. 1897, 125, 23; Hogborn, Bull. Soc. chim. 1881, 35, 61; Wells and Willis, Amer. J. Sci. 1901, 12, 190).

Tellurium hexafluoride TeF_6 , formed by the direct union of its elements, is a gas, slowly decomposed by water. Its molecular weight, determined from its vapour density, is 239, corresponding to the simple formula (Prideaux, Chem. Soc. Trans. 1906, 89, 320; *cf.* Moissan, Ann. Chim. 1891, [vi.] 24, 239).

Tellurium dichloride TeCl_2 , formed by the direct union of its elements, is an almost black substance, which melts at 175° , and boils at 327° , yielding a deep red vapour having the normal density (Michaelis, Ber. 1887, 20, 2488, 2491); for the absorption spectrum of the vapour, *v.* Friederichs, Chem. Zentr. 1905, ii. 1073. The dichloride is decomposed by water into tellurium, tellurous and hydrochloric acids.

The dichloride is only stable in the gaseous condition or in solution and in equilibrium with its decomposition products, tellurium and the tetrachloride. In the solid state it dissociates into a solid solution of the element in the tetrachloride. In ethereal solution it absorbs bromine and iodine, yielding substances which appear to be the chlorobromide and chloriodide respectively (Damiens, Ann. Chim. 1923, 19, 44).

Tellurium tetrachloride TeCl_4 is formed when excess of either chlorine or sulphur chloride (Lenher, J. Amer. Chem. Soc. 1902, 24, 188) acts on tellurium. It is a white crystalline substance, which melts at 224° to a yellow liquid, and boils at 380° , giving a red vapour of normal density (Michaelis, *l.c.*). It is very hygroscopic and is readily hydrolysed by water to tellurous and hydrochloric acids. It forms a large number of additive compounds with metallic chlorides, and also unites with hydrochloric acid (Wheeler, Amer. J. Sci. 1893, [iii.] 45, 267; Weber, Pogg. Ann. 1858, 104, 422; Metzner, Compt. rend. 1897, 125, 23; *cf.* Lenher and Titus, J. Amer. Chem. Soc. 1903, 25, 730; Lenher, *ibid.* 1900, 22, 136).

Tellurium dibromide TeBr_2 , obtained by heating the tetrabromide with tellurium, is a black crystalline substance, melting at 280° , and boiling at 339° ; the vapour is violet. It resembles the corresponding chloride (Brauner, Chem. Soc. Trans. 1889, 55, 410).

Dibromide of tellurium exists in the gaseous state, but is unstable in the solid state. It is an endothermic substance, chocolate-brown in colour, decomposed by water (Damiens, Compt. rend. 1921, 173, 300; Chem. Soc. Abstr. 1921, ii. 546, 636).

Tellurium tetrabromide TeBr_4 , formed by the direct union of the two elements, can be sublimed *in vacuô*. It forms fiery red crystalline crusts when hot, orange yellow when cold; the

density is 4.31. It melts at about 380° , and boils at about 420° , but the vapour undergoes dissociation into the dibromide and bromine. Tellurium tetrabromide dissolves in a small quantity of water, but is readily hydrolysed by an excess. It forms numerous double bromides, *e.g.* K_2TeBr_6 which crystallise beautifully and are easy to prepare (Wills, Chem. Soc. Trans. 1879, 35, 711; Wheeler, Amer. J. Sci. 1893, iii. 45, 267); for compounds of the tetrabromide with organic bases, *see* Lowy and Dunbrook, J. Amer. Chem. Soc. 1922, 44, 614.

Tellurium has been said to form the following compounds with iodine: tellurium diiodide TeI_2 , and tellurium tetraiodide TeI_4 .

Tellurium diiodide TeI_2 does not appear to exist, the substance described by Berzelius being a mixture (Gutbier and Flury, Zeitsch. anorg. Chem. 1902, 32, 108).

From a thermal study of mixtures of tellurium and iodine in varying proportions it is shown that the so-called tellurium diiodide, TeI_2 , is not a definite compound, but is a mixture of two substances, namely, the tetraiodide and a solid solution of tellurium and the tetraiodide. The product, having the composition TeI_2 , when melted and allowed to cool, deposits first of all the tetraiodide at 215° , and on further cooling the eutectic mixture begins to deposit at 170.3° and continues until complete solidification is reached. The curve only indicates one definite compound, the tetraiodide, TeI_4 (Damiens, Compt. rend. 1920, 171, 1140; Chem. Soc. Abstr. 1921, ii. 110).

Tellurium tetraiodide TeI_4 , obtained by heating finely divided tellurium with excess of iodine when the excess of iodine may be extracted from the crystalline mass with carbon tetrachloride, or by the action of hydriodic acid on tellurous acid (*cf.* Gooch and Morgan, Amer. J. Sci. 1896, 2, 271), is an iron-grey crystalline substance of sp.gr. 5.05 at 15° , which melts at 280° and then decomposes. It forms double salts with metallic iodides (Wheeler, *l.c.*); *cf.* Jaeger and Menke, Proc. K. Akad. Wetensch, Amsterdam, 1912, 14, 724.

It is not possible to determine the freezing-point of mixtures containing more than 70 p.c. of tellurium in an open vessel, and mixtures rich in iodine boil. The compound TeI_4 dissociates when heated in carbon dioxide (Jaeger and Menke, Zeitsch. anorg. Chem. 1912, 77, 320; Chem. Soc. Abstr. 1913, ii. 41).

Fusion of iodine with tellurium.—Tellurium products which contain a large excess of iodine have the same vapour pressure as pure iodine at the same temperature. With excess of tellurium, the iodine vapour pressure is very small up to 150° (Wright, Chem. Soc. Abstr. 1916, ii. 29).

Tellurium tetraiodide may readily be prepared in a pure state by heating finely powdered tellurium with an excess of iodine and allowing the mixture to cool slowly. The tetraiodide crystallises out and the excess of iodine may be extracted with carbon tetrachloride. If a further purification is desired, the product is heated in a sealed tube for several hours at 150° – 160° . So prepared, tellurium tetraiodide has m.p. 280° ; D^{15} 5.05. Above 100° , it readily dissociates into tellurium and iodine. The tetraiodide serves as a useful starting material for the preparation of numerous

derivatives of tellurium (Damiens, Compt. rend. 1921, 172, 1105; Chem. Soc. Abstr. 1921, ii. 399).

Tellurium perchlorate $2TeO_2 \cdot HClO_4$ made by dissolving tellurium dioxide in warm concentrated perchloric acid. Glistening hexagonal leaflets. May be heated to 300° without decomposition (Fichter and Schmid, Zeitsch. anorg. Chem. 1916, 98, 141).

Tellurium nitrite is said to be formed by the action of nitric acid upon tellurium as a flesh-coloured precipitate which could be dried at 100° without decomposition. At higher temperatures it is converted into yellow tellurium dioxide. *See* F. von Oefele (Pharm. Zentr. 1920, 61, 491; Chem. Soc. Abstr. 1920, ii. 617).

Tellurium dicyanide $Te(CN)_2$ can be obtained by the interaction of the tetrabromide with silver cyanide in benzene solution (Cocksedge, Chem. Soc. Trans. 1908, 93, 2176). It is decomposed by water.

OXIDES AND OXYACIDS OF TELLURIUM.

Tellurium monoxide TeO is a black powder, obtained by heating $TeSO_3$ to 230° *in vacuo* (Divers and Shimosé, Chem. Soc. Trans. 1883, 43, 319). It dissolves in concentrated sulphuric acid, forming a red solution from which *tellurium sulphate* is said to separate (*cf.* Doolan and Partington, Chem. Soc. Trans. 1924, 125, 1402).

Tellurium dioxide TeO_2 is formed by burning tellurium in air, or by igniting tellurous or telluric acid, and is prepared by oxidising tellurium with warm nitric acid of sp.gr. 1.25 (Klein and Morel, Bull. Soc. chim. 1885, [ii.] 43, 198). It is a white or light yellow crystalline, dimorphous solid, which melts at a red heat and may be slowly sublimed. It is easily reduced to tellurium by hydrogen or carbon. Its vapour introduced into a Bunsen flame gives a blue-coloured flame tinged with green in the upper part and deposits a bright metallic mirror on a cold surface (*cf.* Papish, Chem. Soc. Abstr. 1918, ii. 309). It is practically insoluble in water, but dissolves in alkali hydroxides forming tellurites. The oxide is slightly basic, since it forms a basic sulphate $2TeO_2 \cdot SO_3$ and a basic nitrate $2TeO_2 \cdot HNO_3$ (Klein, Compt. rend. 1884, 99, 326; Ann. Chim. 1887, 10, 108; Norris, Fay and Edgerly, Amer. Chem. J. 1900, 23, 105). Tellurium dioxide has been recommended for the combustion of substances like ferrochrome, calcium cyanamide, &c. (Glauser, Chem. Zeit. 1914, 38, 187; *see also* Zeitsch. angew. Chem. 1921, 34, 154). In the case of ferrosilicon, carborundum, &c., the reaction is very slow, and for such substances lead oxide, or a mixture of lead oxide and tellurium dioxide, should be used.

According to Schluck (Monatsh. 1916, 37, 489) the behaviour of tellurium towards hydrogen peroxide is found to depend on the physical condition of the element. Colloidal tellurium is acted on by very dilute solutions of the peroxide, whilst the crystalline modification only reacts slowly with 60 p.c. hydrogen peroxide at 100° . The rate of dissolution increases with the amount of telluric acid formed. Amorphous tellurium, precipitated from hydrochloric acid solution by sulphur dioxide and dried at 105° , behaves similarly to crystalline tellurium, but

if the amorphous variety is dried by treatment with alcohol and ether, it dissolves quite readily in concentrated hydrogen peroxide solution (Chem. Soc. Abstr. 1916, ii. 615).

Tellurous acid H_2TeO_3 is a light white powder obtained by pouring a solution of tellurium in dilute nitric acid into an excess of water, washing the precipitate and drying it over sulphuric acid. It is slightly soluble in water, and behaves as a weak, dibasic acid; the alkali salts only are soluble in water (Berzelius, Pogg. Ann. 1834, 32, 577; Oppenheim, J. pr. Chem. 1857, 71, 267).

Tellurous acid may also be obtained from the residues from the electrolytic refining of copper as follows: The residues are treated with a solution of ammonium hydroxide and the tellurous acid precipitated from the solution so obtained by means of acetic acid (*cf.* Browning and Flint, Chem. Soc. Abstr. 1909, ii. 934). By dissolving the tellurous acid thus obtained in sodium hydroxide and precipitating again by acetic acid, copper and many other metals, the hydroxides of which are insoluble in sodium hydroxide, are removed.

If the precipitation of the tellurous acid by acetic acid is brought about without warming the solution, and the product is dried without heating, the tellurous acid obtained is readily soluble, in the alkali hydroxides. If, however, the precipitation takes place in hot solution and the precipitate is dried by the application of heat, the product tends to be quite insoluble in the alkali hydroxides.

After the first treatment of the residues with ammonia in this extraction process it was observed that a purple, crystalline salt separated from the alkaline solution on keeping. A similar salt could be obtained by allowing an ammoniacal solution of tellurous acid containing some copper salt to evaporate over sulphuric acid, and in the presence of soda lime; also, by adding slowly, with constant stirring, acetic acid to an ammoniacal solution of tellurous oxide and copper chloride. This salt on analysis gave TeO_2 , 83.84; CuO , 4.63; NH_3 , 5.22; H_2O , 6.10; and is a *copper ammonium tellurite*. Similar salts could not be obtained with nickel, cobalt, zinc, cadmium, or silver in the place of copper (Oberhelman and Browning, Amer. J. Sci. 1913, [iv.] 36, 399; Chem. Soc. Abstr. 1913, ii. 949).

Tellurous acid may be oxidised to telluric acid in either acid or alkaline solution; these reactions are used in its volumetric estimation (Brauner, Chem. Soc. Trans. 1890, 59, 238). It is reduced to tellurium by sulphur dioxide and other reducing agents.

For metallic tellurites *see* Lenher and Wolessky, J. Amer. Chem. Soc. 1913, 35, 718.

Tellurium trioxide TeO_3 is an orange-yellow, crystalline mass of sp.gr. 5.07, obtained by heating telluric acid nearly to redness, and dissolving out any admixed dioxide from the residue by cold hydrochloric acid. It is insoluble in water, dissolves in concentrated potassium hydroxide, and slowly reacts with concentrated hydrochloric acid, being reduced to tellurous acid.

Telluric acid H_2TeO_4 may be obtained by decomposing its barium salt with sulphuric acid,

or by dissolving tellurium in nitric acid and boiling the strongly acid solution with chromic acid; on cooling the solution the dihydrate $\text{H}_2\text{TeO}_4 \cdot 2\text{H}_2\text{O}$ or $\text{Te}(\text{OH})_6$ crystallises out (Staudenmaier, Zeitsch. anorg. Chem. 1895, 10, 189); or by suspending powdered tellurium in water and treating with chlorine evaporating the solution to a small volume and adding acetone or alcohol, when telluric acid is obtained as a crystalline precipitate (Browning and Minnig, Amer. J. Sci. 1913, [iv.] 36, 72; Meyer and Moldenhauer, Zeitsch. anorg. Chem. 1921, 119, 132). This hydrate is dimorphous, crystallising in both the monoclinic and the cubic systems (Gossner, Zeitsch. Kryst. 1904, 38, 498); its density is 3.05. The anhydrous acid is obtained by gently heating the dihydrate.

Telluric acid dihydrate dissolves in cold water very slightly, but is easily soluble in hot water. Sulphur dioxide and other reducing agents reduce it to tellurium. It behaves as a very feeble acid.

Aqueous solutions of telluric acid of all concentrations are slowly reduced by hydrogen sulphide and by sulphur dioxide. In 30 p.c. solution, the acid is reduced by sulphur, selenium, and tellurium when heated in a sealed tube at 110° .

By comparison with selenic acid, telluric acid is not so easily reduced. Although this is not in accordance with the behaviour expected according to the periodic grouping of the elements of the sulphur group, it is in harmony with the thermo-chemical data (Benger, J. Amer. Chem. Soc. 1917, 39, 2179).

Another modification of the acid, *allotelluric acid*, is obtained by heating the dihydrate to 160° for some time; it dissolves very slowly in cold water and is a much stronger acid than the ordinary form (Mylius, Ber. 1901, 34, 2208; *cf.* Brauner, Chem. Soc. Trans. 1895, 67, 549; Gutbier, Zeitsch. anorg. Chem. 1902, 32, 96).

The alkali tellurates are soluble in water; those of the other metals are difficultly soluble in water, but readily soluble in hydrochloric acid (Gutbier and Wagenknecht, *ibid.* 1904, 40, 260; Hutchins, J. Amer. Chem. Soc. 1905, 27, 1157). Besides normal and acid tellurates, more complex salts, *e.g.*

$\text{K}_2\text{TeO}_4 \cdot \text{TeO}_3 \cdot 4\text{H}_2\text{O}$; $\text{K}_2\text{TeO}_4 \cdot 3\text{TeO}_3 \cdot 4\text{H}_2\text{O}$ and $\text{K}_4\text{TeO}_5 \cdot 8\text{H}_2\text{O}$ are known. A number of tellurates exist in two forms, one being white and soluble in water or acids, and the other being yellow and insoluble in these liquids (Berzelius). Complex compounds of telluric acid with iodates, phosphates, &c., are known (Weinland and Prause, Ber. 1890, 23, 1015; Zeitsch. anorg. Chem. 1899, 21, 43; 1901, 28, 45).

The molecular weight of telluric acid in aqueous solution corresponds to the formula $\text{H}_2\text{TeO}_4 \cdot 2\text{H}_2\text{O}$, and it is therefore regarded as having the constitution $\text{Te}(\text{OH})_6$.

Tellurates are reduced to tellurites either by ignition or by boiling with concentrated hydrochloric acid.

Telluric acid and tellurates give a yellow crystalline precipitate of mercurous tellurate with a dilute nitric acid solution of mercurous nitrate (Denigès, Ann. Chim. anal. 1915, 20, 57).

The investigation of telluric acid and its alkali salts has shown that these readily undergo

polymerisation, with the formation of substances of semi-colloidal or colloidal character, according to the degree of polymerisation.

Measurements of the hydrogen ion concentration of 1 *N*-telluric acid solution gave $[H^+] = 4 \times 10^{-5}$ gram-ion per litre. On the assumption that the acid ionises in accordance with the equation $H_6TeO_6 = H^+ + H_5TeO_6'$, this gives $K = 1.6 \times 10^{-4}$ for the ionisation constant. According to this result, telluric acid is a very weak acid, approximating very closely to boric acid and hydrocyanic acid. This is in agreement with the very small value of the molecular conductivity, which increases from 0.1902 for $v=4$ to 0.6193 for $v=1024$ litres per gram-molecule. Freezing-point and boiling-point measurements for telluric acid solutions were also made, and these observations are in general agreement with the evidence afforded by the electrical measurements. Irregularities in the boiling-points were found which are attributed to the formation of modifications of telluric acid of colloidal character. That the constitution of the aqueous solution changes with rise of temperature is shown by the abnormally large value of the temperature coefficient of the molecular conductivity. The fact suggests that the more complex modification formed as the temperature rises is more strongly ionised than the modification which is represented by the crystalline acid. The so-called allotelluric acid described by Mylius, (Chem. Soc. Abstr. 1901, ii. 550) represents such a polymerised modification of greater conductivity. When aqueous solutions of *allotelluric* acid are kept at 25°, the conductivity falls, and ultimately reaches the value which is characteristic of the crystallised acid. The depolymerisation is also shown in other properties of the solution, but the milky appearance indicates that small quantities of a colloidal, insoluble modification are present. In view of this behaviour, it would seem that *allotelluric* acid is not a homogeneous modification, but consists of a mixture of polymerised forms differing considerably in complexity. The investigation of the sodium, lithium, and potassium salts has shown that these behave in many ways like the free acid. These salts have no definite solubility in water; the quantity of water which the crystals contain varies according to the concentration of the solutions from which they are deposited, and the crystals undergo dehydration without any appreciable change in appearance. In these and other respects the salts resemble colloids. They not only absorb water, but experiments made with lithium tellurate show that the basic salts which have been described are in all probability adsorption compounds formed by the adsorption of lithium hydroxide solution. In a similar way, experiments made with potassium tellurate indicate that the so-called acid salts are adsorption compounds containing variable proportions of adsorbed telluric acid. In view of these observations, the statements made with respect to the alkali tellurates in the older literature must be accepted with reserve.

In the course of this investigation, solutions containing telluric acid and potassium nitrate were found to deposit large crystals of the composition $2KNO_3 \cdot H_6TeO_6 \cdot 2H_2O$. This substance can be recrystallised from dilute solutions

of potassium nitrate without decomposition. With silver nitrate, the acid forms the compound $AgNO_3 \cdot H_6TeO_6$.

Reference is made to the fact that telluric acid readily crystallises with other salts, for example, with phosphates, arsenates, iodates, and oxalates. The formation of these additive compounds is supposed to be connected with the weak acid nature of telluric acid (Rosenheim and Jander, *Kolloid. Zeitsch.* 1918, 22, 23; Chem. Soc. Abstr. 1918, ii. 194).

Tellurium sulphoxide $TeSO_3$, obtained by dissolving tellurium in pure sulphur trioxide, is a red amorphous solid, melting at 30°, which is decomposed by water (Weber, *J. pr. Chem.* 1882, [ii.] 25, 218; Divers and Shimosé, *l.c.*).

Tellurium sulphides. The precipitates obtained by passing hydrogen sulphide into solutions of tellurites and tellurates, and which were described by Berzelius as sulphides, are simply mixtures of sulphur and tellurium (Becker, *Annalen*, 1876, 180, 257; Brauner, *Chem. Soc. Trans.* 1895, 67, 545; Gutbier and Flury, *Zeitsch. anorg. Chem.* 1902, 32, 272). The substance initially precipitated from a cold solution of a tellurite appears to be a mixture of TeS and S , the former decomposing on standing (Snelling, *J. Amer. Chem. Soc.* 1912, 34, 802). Hageman (*J. Amer. Chem. Soc.* 1919, 329) finds that TeS_2 is capable of existence at -20° , but gradually dissociates above this temperature, the velocity of dissociation increasing as the temperature is raised. According to Hageman, it is doubtful whether the monosulphide TeS exists under any conditions. No compound has been isolated from fused mixtures of the two elements, which form two series of mixed crystals, and are therefore isodimorphous (Pellini, *Atti R. Accad. Lincei*, 1909, [v.] 18, i. 70; ii. 19; Jaeger, *Proc. K. Akad. Wetensch. Amst.* 1910, 12, 602; Chikashigé, *Zeitsch. anorg. Chem.* 1911, 72, 109). The sulphides appear to exist, however, in colloidal solution (Gutbier, *Zeitsch. anorg. Chem.* 1902, 32, 272, 292) and thiotellurites and thiotellurates have been isolated (Berzelius, *Pogg. Ann.* 1826, 8, 411; Oppenheim, *J. pr. Chem.* 1857, 71, 267).

Tellurium forms compounds with the following metals: with antimony, *see* Kimata (*Mem. Coll. Sci. Kyoto*, 1915, 1, 115; *Chem. Soc. Abstr.* 1916, ii. 39); with antimony and lead, *see* Dreifuss (*Z. Electrochem.* 1922, 28, 100); with gold and silver, *see* Pellini (*Gazz. chim. ital.* 1915, 45, i. 469; *Chem. Soc. Abstr.* 1915, ii. 560; *see also* Chikashige and Saito, *Chem. Soc. Abstr.* 1917, ii. 139); with lead, *see* Kimura (*Mem. Coll. Sci. Kyoto*, 1915, 8, 149; *Chem. Soc. Abstr.* 1916, ii. 34).

For halogeno-salts of tellurium, *see* Gutbier, Flury and Ewald (*J. pr. Chem.* 1912, ii. 86, 150; *Zeitsch. anorg. Chem.* 1914, 86, 169); tellurium hydrogen salts, *see* Hageman (*J. Amer. Chem. Soc.* 1919, 41, 342).

Detection and estimation of tellurium.—Tellurium is precipitated (by reducing agents or by electrolysis) as the element and weighed as such, or else precipitated and weighed as dioxide; numerous volumetric methods have been devised, *v.* ANALYSIS, and Divers and Shimosé, *Chem. Soc. Trans.* 1883, 43, 329; McIvor, *Chem. News*, 1902, 86, 308; 1903, 87, 17; Gutbier, *Zeitsch. anorg. Chem.* 1904, 41, 448; 1902, 32,

260, 295; Pellini, Atti R. Accad. Lincei, 1903, 12, ii. 312; 1904, 13, ii. 275; Gallo, *ibid.* 1904, 13, i. 713; Pellini, Gazz. chim. ital. 1903, 33, i. 515; Brauner and Kuzma, Ber. 1907, 40, 3362; Lenher and Homberger, J. Amer. Chem. Soc. 1908, 30, 387; Perkins, Amer. J. Sci. 1910, 29, 540; Gutbier and Huber, Zeitsch. anal. Chem. 1914, 53, 430. For the detection of tellurium in presence of selenium, *see* Dennis and Koller (J. Amer. Chem. Soc. 1919, 41, 949). For the cathodic deposition of tellurium and selenium from their oxy-acids and their electroanalytical estimation, *see* Müller, Menzel and Schubert (Chem. Soc. Abstr. 1922, ii. 390).

The qualitative detection and separation of platinum, arsenic, gold, selenium, tellurium, and molybdenum, *see* Browning (Amer. J. Sci. 1915, [iv.] 40, 349).

For the qualitative separation and detection of tellurium and arsenic, and of iron, thallium, zirconium, and titanium, *see* Browning, Simpson and Porter (Chem. Soc. Abstr. 1916, ii. 536).

The ternary system tellurium tetra-iodide—hydrogen iodide—iodine, and the estimation of tellurium by means of hydrazine hydrate, *see* Menke (Zeitsch. anorg. Chem. 1912, 77, 282; Chem. Soc. Abstr. 1913, ii. 41).

See Hulot (Chem. Soc. Abstr. 1920, ii. 174) for the estimation of tellurium in tetradymite.

Potassium dichromate titration can be applied successfully to the volumetric estimation of tellurium. Tellurium dioxide in hydrochloric acid solution is oxidised quantitatively to tellurium trioxide by potassium dichromate. The weight of tellurium dioxide should be less than 0.3 gram, and the solution should contain 2.0 p.c. of free hydrochloric acid. The volume of the solution should be approximately 200 c.c. The titration is carried out as follows: To the acid solution of tellurium dioxide an excess of 0.1N potassium dichromate solution is added, followed in half an hour by a known excess of standard ferrous sulphate solution, the excess of which is subsequently titrated by dichromate, using ferricyanide as an indicator (Lenher and Wakefield, J. Amer. Chem. Soc. 1923, 45, 1423–1425; J. Chem. Soc. Abstr. 1923, 123, 124; ii. 576).

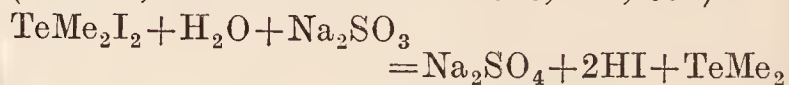
Flame reactions of tellurium.—The element tellurium, as well as its dioxides and hydrides, have been introduced into the hydrogen air flame and the colour changes observed. At the same time experiments were made to ascertain the nature of the deposit, if any, on a cold object introduced into the flame. Tellurium dioxide, hydrogen telluride, and tellurium all produce a lilac luminescence in the middle zone and a green luminescence in the outer zone, whilst tellurium dioxide and the free element produce a green luminescence in the inner zone, whereas the hydrogen telluride produces a blue luminescence in this region (Papish, Zeitsch. physikal. Chem. 1918, 22, 640; Chem. Soc. Abstr. 1919, ii. 105; *see also* Weiser and Garrison, Zeitsch. physikal. Chem. 1919, 23, 478; Chem. Soc. Abstr. 1919, ii. 509).

ORGANIC DERIVATIVES.

Orthotelluric acid methyl ester $\text{Te}(\text{OMe})_6$ white shining laminae, m.p. 85°–87°. Decomposed by water (*cf.* Pellini, Gazz. chim. ital. 1916, 46, ii. 247; Chem. Soc. Abstr. 1917, i. 2).

Diethyl telluride $\text{Te}(\text{C}_2\text{H}_5)_2$ *v.* ETHYL.

Dimethyl telluride $\text{Te}(\text{CH}_3)_2$, obtained from methyl barium sulphate and potassium telluride, is a pale-yellow oil, with a garlic odour (Wöhler and Dean, Annalen, 1855, 93, 233; Heeren, *l.c.*; Demarçay, Bull. Soc. chim. 1883, [ii.] 40, 100; Scott, Chem. Soc. Proc. 1904, 20, 157). It is best obtained by gently heating TeMe_2I_2 with sodium sulphite in presence of sodium carbonate (Vernon, Chem. Soc. Trans. 1920, 117, 892)

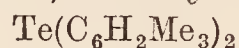


It boils at 94°/770 mm. and solidifies in liquid air. With water in presence of air it yields $\text{TeMe}_2(\text{OH})_2$. For other derivatives *see* Vernon, *l.c.*, and Chem. Soc. Trans. 1921, 687.

Diphenyl telluride $(\text{C}_6\text{H}_5)_2\text{Te}$ is obtained by heating mercury diphenyl with tellurium (in CO_2). It is a liquid, boiling at 312°–320°. The *dibromide* forms small yellow prisms, melting at 203.5°; it is converted into the *oxide* by warming with sodium hydroxide (Krafft and Lyons, Ber. 1894, 27, 1769; Pellini and Menin, Gazz. chim. ital. 1900, 30, ii. 472).

Diphenyl ditelluride, long red fibres, m.p. 53°–54°, Lederer, Ber. 1915, 48, 1345.

Dimesityl telluride. According to Lederer (Ber. 1916, 49, 345) *dimesityl telluride*



was obtained by the action of tellurium dibromide on magnesium mesityl bromide in crystals, m.p. 129°, and converted into the following telluronium compounds: *dichloride*, needles, m.p. 178°–179°; *dibromide*, small yellow needles, m.p. 205°–206° (decomp.); *di-iodide*, very deep red columns, m.p. 111°; *oxide*, $\text{TeO}(\text{C}_6\text{H}_2\text{Me}_3)_2$, m.p. 204°–205°; and *anhydride* of a *basic iodide* $(\text{C}_{18}\text{H}_{22}\text{TeI})_2$, m.p. 100° (Chem. Soc. Abstr. 1916, i. 393).

Di- α -naphthyl telluride $\text{Te}(\text{C}_{10}\text{H}_7)_2$ melts at 126.5°; the *dichloride* and *dibromide* of this compound melt at 265° and 244° respectively (Lyons and Bush, J. Amer. Chem. Soc. 1908, 30, 831).

Di- α -naphthyl telluride was obtained by Lyons and Bush by heating tellurium with mercury di- α -naphthyl (Chem. Soc. Abstr. 1908, i. 417), but it may also be obtained by the action of magnesium α -naphthyl bromide on tellurium dibromide. It forms *additive compounds* with the mercuric halides: *chloride*, m.p. 187°–188° (decomp.); *bromide*, m.p. 178°–179°; *iodide*, yellow granules, m.p. 152°–153° (decomp.). *Di- α -naphthyltelluronium di-iodide* crystallises in deep red needles, m.p. 184°–186°; the *oxide*, R_2TeO , is a microcrystalline powder, m.p. 224°–225° (decomp.), and *di- α -naphthylmethyltelluronium iodide* has m.p. 146° (decomp.) (Lederer, Ber. 1916, 49, 2663).

Di-*o*-anisyl telluride has been prepared by the action of magnesium *o*-anisyl bromide on tellurium dibromide; it is purified by conversion into the crystalline *dibromide*, and reduction of the latter with magnesium methyl iodide.

Di-*o*-anisyl telluride $\text{Te}(\text{C}_6\text{H}_4\text{OMe})_2$ is a colourless, crystalline substance, m.p. 73°–74°, b.p. 248°–251°/30 mm., which gives rise to the following *di-*o*-anisyltelluronium* compounds in the usual way: *dichloride*, microscopic rods, m.p. 184°–185°, after softening at 182°; *dibromide*, small monoclinic platelets, m.p. 195°–

196°, after softening at 192°; *di-iodide*, shining, metallic, iodine-coloured needles, m.p. 199°–200°, after softening at 198°; *oxide*,



needles, m.p. 205°–206°; *methiodide*, small rods, m.p. 124°–125°. It also forms *additive* compounds with mercuric haloids, as follows: *iodide* $\text{Te}(\text{C}_6\text{H}_4\cdot\text{OMe})_2\cdot\text{HgI}_2$, yellow crystals, m.p. 80°–81°, after softening at 79°; *bromide*, yellow crystals, m.p. about 84°, after softening at 70°; *chloride*, obtained as an oil, which, after solidification, has m.p. 143°–144°, and recrystallisation has m.p. 156°–157° (decomp.) after softening at 150° (Lederer, Ber. 1920, 53, [B] 712; Chem. Soc. Abstr. 1920, i. 482).

Di-*m*-anisytelluride has been prepared by the action of magnesium *m*-anisyl iodide on tellurium dibromide; it is purified by conversion into the crystalline dibromide and reduction of the latter with magnesium methyl iodide.

Di-m-anisyltelluride $\text{Te}(\text{C}_6\text{H}_4\cdot\text{OMe})_2$ is a pale yellow oil, b.p. 247°–252°/34–36 mm., which gives rise to the following *di-m-anisyltelluronium* compounds in the usual way: *dichloride*, slender felted needles, m.p. 162°–163°; *dibromide*, small felted needles, m.p. 185°–186°; *di-iodide*, minute golden-yellow needles, m.p. 167°–168° (decomp.), after softening at 163°; *oxide* $\text{TeO}(\text{C}_6\text{H}_4\cdot\text{OMe})_2$ amorphous powder, which softens at 69°, and is completely molten at 90°; *methiodide*, not obtained in the pure condition. It also forms *additive* compounds with the mercuric halides as follows: *iodide* $\text{Te}(\text{C}_6\text{H}_4\cdot\text{OMe})_2\cdot\text{HgI}_2$, yellow needles, m.p. 122°–123°, after softening at 120°; *bromide*, needles, m.p. 114°–115° (decomp.), after softening at 108°; *chloride*, colourless amorphous powder which softens at 83° and is completely molten at about 89° (Lederer, Ber. 1919, 52, [B] 1989; Chem. Soc. Abstr. 1920, i. 40).

Di-*o*-phenetyl telluride. According to Lederer (Ber. 1916, 49, 2532), *di-o*-phenetyl telluride has been obtained by the action of magnesium *o*-phenetyl bromide on tellurium dibromide (*cf.* Chem. Soc. Abstr. 1916, i. 208). It is not identical with the Rush-Rohrbach product of the action of tellurium tetrachloride on phenetole (*ibid.*).

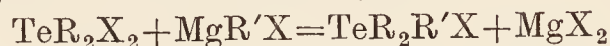
Di-o-phenetyl telluride $\text{Te}(\text{C}_6\text{H}_4\cdot\text{OEt})_2$ is a viscous oil, b.p. 244°–244.5°/18 mm., which gives rise to the following *di-o-phenetyltelluronium* compounds in the usual way: *dichloride*, columns, m.p. 163°–164°; *dibromide*, four-sided columns, m.p. 183°–184°; *di-iodide*, deep reddish-brown needles or rhombic tablets, m.p. 214°–215°; *oxide* $\text{TeO}(\text{C}_6\text{H}_4\cdot\text{OEt})_2$, short needles, m.p. 205°–206°, easily oxidised by the air during its crystallisation; *methiodide*, columns, m.p. 138°–140°. It also forms *additive* compounds with the mercuric haloids, as follows: *chloride* $\text{Te}(\text{C}_6\text{H}_4\cdot\text{OEt})_2\cdot\text{HgCl}_2$, m.p. 174°–175°; *bromide*, m.p. 160°–161°; *iodide*, m.p. 90° (Chem. Soc. Abstr. 1917, i. 134).

Triphenyl- and tri-tolyl-telluronium salts were prepared by the action of the magnesium aryl halides on tellurium tetrachloride.

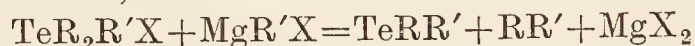
The *tri-m-tolyltelluronium* salts $\text{TeX}(\text{C}_7\text{H}_7)_3$ are as follows: *iodide*, scales, m.p. 160°–161°; *picrate*, small needles, m.p. 152°–153°; *double salt* with mercuric chloride, $\text{TeCl}(\text{C}_7\text{H}_7)_3\cdot\text{HgCl}_2$, white leaflets, m.p. 159°–160°. *Tri-p-xylyl-5-*

telluronium iodide forms elongated, four-sided leaflets, m.p. 186°–187°; *tri-m-xylyl-4-telluronium iodide* crystallises in colourless needles, m.p. 208°–209°, and the *picrate* has m.p. 138°–139°. *Tri-p-anisyltelluronium iodide* is a crystalline powder, m.p. 160°, and the *picrate* forms rhombic tablets, m.p. 160°. *Trimesityltelluronium iodide* crystallises in small, white needles, m.p. 169°–170°, and the *bromide* has m.p. 164° (Lederer, Ber. 1916, 49, 1385; Chem. Soc. Abstr. 1916, i. 810).

Triaryltelluronium halides are conveniently prepared by the action of Grignard agents on diaryltelluronium dihaloids, thus:



and mixed with triaryltelluronium halides can be reduced by treatment with a further quantity of an organomagnesium salt to mixed diaryl tellurides, thus:



For example, *di-p-tolyltelluronium* dichloride and magnesium phenyl bromide (1 mol.) yield a compound which is precipitated by the addition of potassium iodide as *phenyldi-p-tolyltelluronium iodide*. This crystallises in tetragonal columns, m.p. 209°–210°, whilst the corresponding *bromide* forms small nodules, m.p. 230°–231°, and the *picrate* rosettes of yellow, rhombic platelets, m.p. 132°–133°. For the preparation of the phenyl tolyl telluride, the ditolyltelluronium dichloride may be treated directly with an excess (5 mols.) of magnesium phenyl bromide, and the crude dibromide which separates deprived of bromine by means of sodium hydrogen sulphite.

Phenyl-*p*-tolyl telluride $\text{TePh}\cdot\text{C}_7\text{H}_7$ crystallises in slender needles, m.p. 63°–64°, b.p. 207°–208°/16 mm., and yields the following *phenyl-p-tolyltelluronium* compounds: *dichloride*, needles, m.p. 135°–136°; *dibromide*, m.p. 175°–176°; *di-iodide*, reddish-brown columns, m.p. 195°, or carmine red needles, m.p. 204°; *oxide*, white granules; *anhydride* of the *basic chloride* $(\text{TeRR}'\text{Cl})_2\text{O}$, microscopic columns, m.p. 243°–244°; *anhydride* of the *basic bromide*, m.p. 259°–260°; *basic iodide*, $\text{TeRR}'\text{I}\cdot\text{OH}$, a yellow, amorphous powder, m.p. 200°–201°. The telluride also reacts with methyl iodide to form *phenyl-p-tolylmethylytelluronium iodide*, m.p. 73°–74°, and yields *double salts* with the mercuric halides (*chloride* $\text{TeRR}'\cdot\text{HgCl}$, a white powder, m.p. 91°; *bromide*, m.p. 54°; *iodide*, m.p. 74°) (Lederer, Ber. 1916, 49, 1615; Chem. Soc. Abstr. 1916, i. 809).

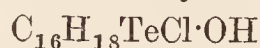
Two ortho-substituted tellurides, namely, *di-p-xylyl* and *di-m-4-xylyl telluride*, have been prepared and their behaviour towards halogens has been studied in extension of the investigation of the phenyl and tolyl tellurides (Chem. Soc. Abstr. 1912, i. 852).

Di-*p*-xylyl telluride $\text{Te}(\text{C}_6\text{H}_3\text{Me}_2)_2$ was prepared by the action of tellurium dibromide on magnesium *p*-xylyl bromide, and separated from the accompanying *di-p-xylyl* by distillation. It formed silky needles, m.p. 72°, b.p. 260°–275°/34 mm., and combined directly with the halogens in ethereal solution. *Di-p-xylyl-telluronium dichloride* $\text{TeCl}_2(\text{C}_6\text{H}_3\text{Me}_2)_2$, crystallised in small colourless needles, m.p. 197°–198°; the *dibromide*, in yellow needles, m.p. 189°–190°; and the *di-iodide*, in deep reddish-

brown needles, m.p. 161°–162°. The dibromide yielded *di-p-xylyl-telluronium oxide*



a microcrystalline powder, m.p. 225°–226°, when heated with dilute sodium hydroxide. When boiled with water, the dichloride and dibromide were gradually hydrolysed, but it was not possible to obtain basic products; a compound, m.p. 227°, which approximates to the constitution of an anhydride of



and reacts with potassium iodide to give the corresponding iodine derivative is described. The telluride also combined with methyl iodide to form *di-p-xylyl-methyltelluronium iodide*, $\text{TeMeI}(\text{C}_6\text{H}_3\text{Me}_2)_2$, m.p. 137° (decomp.), from which the *picrate*, m.p. 170°, was prepared. Double salts with mercuric halides were also obtained: *mercurichloride*, $\text{Te}(\text{C}_6\text{H}_3\text{Me}_2)_2\cdot\text{HgCl}_2$, columns, m.p. 179°–180°; *mercuri-bromide*, broad needles, m.p. 169°–170°; *mercuri-iodide*, golden-yellow needles, m.p. 166°–167°.

Di-m-4-xylyl telluride was obtained as a faintly yellow oil, b.p. 202°–203°/10 mm.; by treating magnesium *m-xylyl* bromide with tellurium dibromide, converting the crude telluride into its dibromide, and reducing this again by means of magnesium methyl iodide. The following derivatives were prepared: *dichloride*, microscopic columns, m.p. 187°–188°; *dibromide*, microscopic yellow prisms, m.p. 200°–201°; *di-iodide*, ruby-red columns, m.p. 181°–182°; *mercurichloride*, m.p. 160°; *mercuribromide*, m.p. 99°; *mercuri-iodide*, yellow scales, m.p. 107°–108°; *di-m-4-xylyl-telluronium oxide*, m.p. 216°–217°; and the product of the action of boiling water on the dichloride, namely, the anhydride of the basic chloride $(\text{C}_{16}\text{H}_{18}\text{TeCl})_2\text{O}$, m.p. 239°–240° (Lederer, Ber. 1916, 49, 334; Chem. Soc. Abstr. 1916, i. 392).

For the *chloride*, *bromide*, and *iodide* of tellurium triphenyl, and their derivatives, *v. Lederer*, Compt. rend. 1910, 151, 611; *see also Rust*, Ber. 1897, 30, 2828; *Rohrbaech*, Annalen, 1901, 315, 9; *Lederer*, Ber. 1915, 48, 2049.

For diphenylaryltelluronium salts, *see Lederer* (Ber. 1920, 53, [B] 1430).

For other organic compounds of tellurium, *see Lederer* (Ber. 1920, 53, [B] 1674); *Vernon* (Chem. Soc. Trans. 1920, 117, 86, 889; *Giua and Cherchi* (Chem. Soc. Abstr. 1920, 117, i. 691); *Knaggs and Vernon* (Chem. Soc. Trans. 1921, 105).

For tellurium organic compounds with arsenic derivatives, *see Farbwerke vorm. Meister, Lucius and Brüning* (Chem. Soc. Abstr. 1914, A, i. 609); tellurium acetylacetone and its derivatives, *see Morgan and Drew* (Chem. Soc. Trans. 1920, 1456; 1921, 610).

See Morgan and Drew for tellurium bisacetylacetone dichloride (Chem. Soc. Trans. 1922, 929); tellurium bisbenzoylacetone dichloride (*ibid.* 930); tellurium bischloroacetylacetone dichloride (*ibid.* 936); tellurium bispivalylacetone dichloride (*ibid.* 938); tellurium chloroacetylacetone and its dichloride (*ibid.* 935); tellurium dibenzoylmethane trichloride (*ibid.* 939); tellurium 3-ethylacetylacetone and its dihalides (*ibid.* 932); tellurium *o*-ethylpivalylacetone

trichloride (*ibid.* 937); tellurium 3-methylacetylacetone and its dihalides (*ibid.* 931).

For compounds of platinum and organic tellurides, *see Fritzmann* (Chem. Soc. Abstr. 1915, i. 644). For the action of methyl iodide on aromatic tellurides, *see Lederer* (Chem. Soc. Abstr. 1913, i. 1182). The action of nitric acid on aromatic tellurides, *see Lederer* (Chem. Soc. Abstr. 1916, i. 647). For salts of mercuric chloride with aromatic tellurides, *see Lederer* (*ibid.* 1914, i. 275).

TELLURIUM OCHRE *v.* TELLURIUM.

TEMISKAMITE. This mineral occurs with niccolite, bismuth, and silver in calcite veins in the Moose Horn Mine, Elk Lake, Ontario. It is silver-white with a tinge of red and a metallic lustre; on exposure it tarnishes quickly to madder-grey; streak, brownish-black, H. 5½, D. 7.901. It forms radiating fibrous masses with a botryoidal or arborescent surface. It is slowly attacked by hydrochloric acid, but readily by nitric acid, and is easily fusible. Analysis gives the formula Ni_4As_3 , which is near to that of maucherite (Chem. Soc. Abstr. 1913, ii. 516).

Ni	Co	Fe	As	S	Sb	Bi	Total.
49.07	1.73	trace	46.34	1.03	n.d.	0.55	98.72

(Walker, Amer. J. Sci. 1914, [iv.] 37, 170; Chem. Soc. Abstr. 1914, ii. 210).

TEMPER. An alloy of arsenic and lead sometimes used for hardening shot, *v. ARSENIC*, ALLOYS OF; also **TIN**.

TEMPER-CARBON is the name given to the carbon liberated during the tempering of steel. The change consists in the formation of a conglomerate of temper-carbon, ferrite and pearlite from a mixture of pearlite and cementite. It is identical with ordinary graphite (Charpy, Compt. rend. 1907, 145, 1173).

TENAX. A zinc alloy containing Cu 2.56 p.c. ± 0.35 ; Al 4.42 p.c. ± 0.2 ; Pb up to 1.2 p.c., and Fe up to 0.35 p.c. Has a tensile strength of 7114 kgs. per sq. cm. and an impact test number of 9.06.

TENNANTITE *v.* FAHL-ORE.

TENORITE *v.* MELACONITE.

TENOSIN *p*-oxyphenylethylamine.

TERBIUM. Sym. Tb. At.wt. 159.2. This extremely rare element is present as oxide in the terbia earths which form a connecting link between the more basic cerite earths and the less basic ytterbite earths. The crude 'terbia' consists mainly of gadolinia, but it owes its characteristic yellow colour to the presence of small quantities of terbium peroxide. The existence of this elusive element, terbium, was first indicated by Mosander in 1843, but more than 60 years elapsed before its oxide and salts were isolated in a purified condition.

Occurrence.—In small quantities in monazite, cerite, ytterbite (gadolinite), samarskite, äschy-nite, and other minerals containing the rare earths (*v. CERITE EARTHS*).

Separation and purification. The most soluble portions of the double ammonium or magnesium nitrate fractionation (*v. NEODYMIUM*) form a convenient starting-point for the separation of the three metals of the terbium group, namely, europium, gadolinium, and terbium. A preliminary separation of the cerite metals with potassium sulphate is not to be recommended,

since appreciable amounts of the terbium metals are co-precipitated with the sparingly soluble double sulphates.

Methods of separation based on (1) fractional precipitation with ammonia, (2) fractional crystallisation of double sulphates, ethyl sulphates, oxalates or formates lead rather to a concentration of the terbium group than to a separation of its components, the chief constituent gadolinium being the only one isolated in a moderately pure state by any of these processes (*cf.* EUROPIUM and GADOLINIUM).

The separation of terbium from gadolinium was first accomplished by crystallising repeatedly the double nickel nitrates and then precipitating the bases fractionally with ammonia. In this way 7 grms. of pure terbia were obtained (Urbain, *Compt. rend.* 1904, 139, 736; 1905, 141, 521).

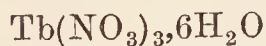
Fractionation of the double magnesium nitrates of the terbia-yttria group from monazite, followed by an application of the basic salt method (*v.* SCANDIUM), and final repeated crystallisation of the oxalates lead to a separation of terbium (Feit, *Zeitsch. anorg. Chem.* 1905, 43, 267).

The nitrates of gadolinium and terbium, unlike the other salts of these metals, differ somewhat widely in solubility. Bismuth nitrate, which is more soluble in nitric acid than gadolinium nitrate, and slightly less soluble than terbium nitrate, is added in excess to an acid solution of the two salts. A complete separation of gadolinium and terbium is effected by fractional crystallisation of the mixture. The terbia thus isolated is identical with the products obtained in the foregoing separations, and its metal is identical with the elements provisionally indicated by the symbols Z_{δ} , Z_{β} (Lecoq de Boisbaudran), Γ (Demarçay), and G_{β} (Crookes).

According to James and Bissel (*J. Amer. Chem. Soc.* 1914, 36, 2060) terbium may be rapidly separated from gadolinium by fractional crystallisation of the bromates.

Terbium oxide (*terbia*) Tb_2O_3 is white and the terbium salts with colourless acid radicles are themselves colourless.

Terbium peroxide Tb_4O_7 , dark-brown or black mass produced by heating terbium oxalate or sulphate respectively; it dissolves in mineral acids to form the following salts which are neutral to litmus: **terbium nitrate**



m.p. 89° , monoclinic crystals; **terbium sulphate** $Tb_2(SO_4)_3 \cdot 8H_2O$, micaceous lamellæ; **terbium chloride** $TbCl_3 \cdot 6H_2O$, very hygroscopic, transparent, prismatic crystals.

Spectra.—Absorption spectrum, 1 band ($\lambda 488$) in blue, and 9 in ultra-violet (*Compt. rend.* 1904, 139, 1015). Spark spectrum, very complex (*ibid.* 1906, 142, 957; *Sitzungsber. Akad. Berlin*, 1906, 384).

Pure terbia gives no cathode luminescence, but traces of this oxide mixed with gadolinia and alumina produce respectively a green and white luminescence, the latter effect being remarkably striking. A mixture of air and gas directed upon terbium peroxide or upon gadolinium oxide containing terbium peroxide, heated nearly to redness, causes incandescence, the gas usually taking fire.

G. T. M.

TEREBENE *v.* OILS, ESSENTIAL; and TERPENES.

TEREBIC ACID *v.* LACTONES.

TEREPHTHALIC ACID *v.* PHTHALIC ACID.

TERPENES. The term 'terpene' was formerly exclusively applied to unsaturated hydrocarbons having the empirical formula $C_{10}H_{16}$, which exist widely diffused in the vegetable kingdom as constituents of various essential or volatile oils. Of these, essence, oil, or spirit of turpentine is one of the most characteristic and best known. The term is now extended to include terpenes $C_{10}H_{16}$, produced by artificial synthetical processes, and also the sesquiterpenes and polyterpenes.

The terpenes in nature are associated with products which have probably been formed from them, or simultaneously with them by polymerisation, oxidation, or the action of water and acids. These products are often of greater importance as perfumes or medicinal agents than the terpenes with which they are diluted, as, for example, in such cases as the essential oils of lemon, bergamot and other fruits of the natural order *Aurantiaceæ*, the essences extracted from the mints and other plants of the *Labiataæ*, those of caraway and other fruits of the *Umbelliferæ*. On the other hand, the varieties of spirit of turpentine obtained from the wood, leaves, or fruits of various *Coniferæ* are of great practical importance as solvents, and in the production of paints and varnishes. An investigation has been made by Sigmund (*Biochem. Zeitsch.* 1924, 146, 389) of the influence of various essential oils and terpenes on the germination of the seeds of the vetch, wheat, and rape plants. Of the oils, that of mustard proved most toxic, whilst clove and caraway oils came next in order, and the oils of aniseed, fennel, geranium, peppermint, rosemary, and thyme, although less active than the first three, definitely inhibited germination. Oil of garlic was toxic in the form of vapour, but much less so in solution, and turpentine oil gave similar results. The oils of bergamot, cedar, lemon, eucalyptus, rue, and juniper berry were practically devoid of effect in solution. The results obtained with the individual constituents of the oils were as follows: cymene, *d*- and *l*-limonene, *d*- and *l*-pinene, styrene, borneol, linalool, menthol, and terpene hydrate were inactive. Terpincol was toxic. Of the aldehydes, benzaldehyde, citral, and cinnamic aldehyde were very toxic, anisaldehyde was somewhat less toxic, and isovaleraldehyde and vanillin were the least toxic. The ketones showed diminishing toxicity in the order given: carvone, camphor, fenchone, cineol. Carvacrol, thymol, apiole, and safrole were very toxic; anethole was feebly toxic. Anisic acid had little or no action. Methyl salicylate was toxic (*J. Soc. Chem. Ind.* 1924, 43, B. 723) (*v.* OILS, ESSENTIAL).

For the purposes of this article it will be convenient to restrict the name *terpene* to the alicyclic hydrocarbons $C_{10}H_{16}$. The name *sesquiterpene* may be applied to compounds of the formula $C_{15}H_{24}$, and the name *polyterpene* to the more complex polymerides $C_{30}H_{48}$, &c.

Compounds containing more than 16 atoms of hydrogen to 10 atoms of carbon may be called *hydroterpenes*.

The natural terpenes are generally liquids

having a characteristic odour, not sensibly soluble in water, and of lower density than water, to which they communicate their peculiar taste and odour (Distilled Waters of Pharmacy). They are miscible to a large though limited extent with alcohol and miscible in all proportions with glacial acetic acid. The natural terpenes are all optically active, some being dextro- and others lævo-rotatory.

Spirit of turpentine has been known for ages as obtainable by distillation with water of the natural exudation from various pine and fir trees. One of the first recorded facts relating to the chemistry of the terpenes is the production of the solid hydrochloride by passing hydrogen chloride into turpentine oil (Kind, Troms-dorff's Journ. d. Pharmacie, xi. pt. ii. 132, 1803). This was for a long time confused with common camphor, and is still sometimes referred to as 'artificial camphor.'

It was not until Liebig's process for the analysis of organic compounds had been perfected that the composition of spirit of turpentine was known, and it was shown that essence of lemon has the same formula (Dumas, Annalen, 1833, 6, 245; also Blanchet & Sell, *ibid.* 262).

It was known that the terpene from essence of lemon boils at a temperature about 20° higher than the b.p. of spirit of turpentine, but down to about 1876 it was supposed that there was an indefinitely large number of hydrocarbons of the same formula $C_{10}H_{16}$, and no classification had been attempted. Tilden and Shenstone then obtained the nitrosochlorides (Chem. Soc. Trans. 1877), and from a study of these compounds Tilden divided the then known terpenes into three classes (Chem. Soc. Trans. 1878) as follows: (1) turpentines or terpenes proper, (2) citrenes or limonenes, (3) sylvestrene, discovered by Atterberg (Ber. 10, 1202). The terpenes are now usually classified in the following groups: (1) the monocyclic terpenes (menthadienes), (2) the bicyclic terpenes, (3) the tricyclic terpenes, (4) the sesquiterpenes, and (5) the polyterpenes. Since 1885 the terpenes and their derivatives have been studied by many chemists. The most important systematic researches are those of O. Wallach (Annalen, 225, &c.), A. von Baeyer (Ber. 26, &c.) and W. H. Perkin, junr. (Chem. Soc. Trans. 1904, &c.).

The several hydrocarbons will now be described under the names which have been, for the most part, introduced by Wallach.

MONOCYCLIC TERPENES (Menthadienes).

1. Limonene.

Dextro-limonene, b.p. 175°–176°, sp.gr. 0.846 at 20°. When obtained from oil of orange $[\alpha]_D = +106.8^\circ$ ca. (Wallach, Annalen, 252, 145). The pure hydrocarbon obtained by treatment of the tetrabromide with zinc-dust and alcohol has b.p. 177.5°, $d_4^{20} 0.8425$, $[\alpha]_D = +125.3^\circ$ (Godlewsky and Roshanowitsch, J. Russ. Phys. Chem. Soc. 1899, 31, 209). This hydrocarbon constitutes the chief ingredient in oils of bitter orange, bergamot, lemon, and limes; it is also present in oils of carraway, pine needles (*P. sylvestris*?), erigeron, &c.

Lævo-limonene is contained in the oil of

Scotch fir leaves (*P. sylvestris* [Linn.]), sometimes called 'Firwool oil' (Tilden, Chem. Soc. Trans. 33, 83; Wallach, Annalen, 227, 287). A specimen, believed to have been obtained from leaves of *P. picea*, gave b.p. 175°–176°, sp.gr. 0.846 at 20°/20°, $[\alpha]_D = -105^\circ$ (Wallach, *ibid.* 246, 221).

The limonenes are distinguished by giving with hydrogen chloride a liquid monochloride, and a dihydrochloride, m.p. 50°, identical with that obtained from dipentene; also a nitrosochloride $C_{10}H_{16}NOCl$, either by the direct addition of nitrosyl chloride (Tilden and Shenstone) or by action of amyl or ethyl nitrite and hydrochloric acid (Wallach). From the nitrosochloride is obtained a nitroso compound, m.p. 72°, which, when prepared from *lævo*-limonene, is identical in every respect with carvoxime $C_{10}H_{14}N \cdot OH$ from carvone. (For Crystallography v. N. Story-Maskelyne, Phil. Mag. 1879, 132; for a comparison of the rotatory powers of the two limonenes and their derivatives v. Wallach, Annalen, 252, 141). The limonenes are further characterised by the formation of a crystalline tetrabromide $C_{10}H_{16}Br_4$, m.p. 104°–105°, by direct addition of bromine (Wallach, *ibid.* 227, 277).

The nitrosochloride obtained as described above either from dextro- or *lævo*-limonene is always a mixture of two compounds, which are separable from each other by means of cold chloroform in which the α -compound is more soluble than the β -. The former crystallises from ether in large clear crystals, the latter in needles. There is a slight difference of melting-point, and the α -compound has in each case a greater rotatory power than the β -. α -Nitrosochloride, m.p. 103°–104°, $[\alpha]_D = +$ or -314° (Conrady, Annalen, 252, 145). β -nitrosochloride, m.p. 105°–106°, has $[\alpha]_D = +$ or -241° ca. Wallach has traced the characters of some of the nitrolamines derived from the two nitrosochlorides, and finds that those derived from the α -compound are identical with those from the β -compound (Annalen, 252, 113). The corresponding nitroso-cyanides, however, do not appear to be the same, neither do the products formed by the action of magnesium methyl iodide on the α - and β -nitrosochlorides respectively (Tilden and Shephard, Chem. Soc. Trans. 89, 920; also Tilden and Leach, *ibid.* 85, 931).

Dipentene (limonene) is the racemic compound formed by mixing together equal quantities of dextro- and *lævo*-limonenes. Just as racemic acid and its salts differ in some physical characters from tartaric acid and the tartrates, so dipentene differs in some respects from the limonenes. Although the boiling-point of the inactive mixture is nearly the same as that of the limonenes, such differences as the following are observed in the melting-points of derivatives:—

	Limonene	Dipentene
Tetrabromide $C_{10}H_{16}Br_4$	105°	126°
<i>d</i> or <i>l</i> -Carvoxime $C_{10}H_{14}NOH$	72°	93°

&c. (Wallach, Ber. 1891, 24, 1559).

The name 'dipentene' includes diisoprene, isoterebenthene, formed by the action of heat on terebenthene, cinene, cajeputene, and also caoutchene, one of the products of the destructive distillation of caoutchouc (*q.v.*).

Dipentene is produced, together with terpinene, terpinolene, and terpineol by the action of sulphuric or phosphoric acid on terpin, or by the action of sulphuric acid on the pinenes under certain conditions. The product thus obtained was formerly called 'terpilene.' Dipentene may be prepared from the dihydrochloride, m.p. 50°, obtained from either limonene or moist pinene, by the action of heat on the chloride (Tilden, Ber. 12, 1133), or by boiling it with a mixture of sodium acetate and acetic acid, or with alcohol and aniline (Wallach). Dipentene thus obtained is, however, accompanied by considerable quantities of cymene, terpinene, terpinolene, together with a small amount of a saturated hydrocarbon of boiling-point 155° (Tilden, Chem. Soc. Trans. 1893). The foregoing methods are all artificial; among the natural products in which dipentene is known to exist are the volatile oils of the camphor tree (Wallach, Annalen, 227, 296), also oil of elemi, and in Russian and Swedish turpentine (Wallach), and many other essential oils.

When prepared from the dihydrochloride with the utmost care by the action of aniline, dipentene appears to be accompanied with another hydrocarbon, perhaps ψ -limonene, which raises the boiling-point to 177°–178° (Wallach, Ber. 1907, 40, 600).

Dipentene, like the limonenes, unites with only one molecule of hydrogen chloride when presented in the form of the dry gas; in the presence of moisture all unite with 2HCl to produce the optically inactive saturated compound $C_{10}H_{16}2HCl$, m.p. 50°, which is identical with the dihydrochloride, formed under the same circumstances from pinene.

Dipentene yields a nitrosochloride, m.p. 101°–102°, which, like the corresponding compounds from the limonenes and from pinene, is bimolecular. It yields an inactive carvoxime, m.p. 93°, which may be formed by mixing together equal weights of *lævo*carvoxime, m.p. 72°, from dextrolimonene and dextrocarvoxime, m.p. 72°, from *lævo*limonene. This compound, notwithstanding the difference of melting-point, gives by Raoult's method a molecular weight corresponding to the simple formula $C_{10}H_{15}NO$ (Wallach, Annalen, 246, 230).

When α -limonene nitrosochloride (*v. Limonene*), prepared from either dextro- or *lævo*limonene, is warmed with an alcoholic solution of piperidine, a mixture of two crystallisable nitrolamines results in each case, as follows:

Nitrolpiperidines $C_{10}H_{16} \cdot NO \cdot NC_5H_{10}$.

From lævolimonene.

α -compound, m.p. 93°–94°. Rhombic (from alcohol). $[\alpha]_D = -67.60$. Hydrochloride *dextro*-rotatory.

β -compound, m.p. 110°–111°. Monosymmetric. $[\alpha]_D = +60.18$. Hydrochloride almost inactive.

From dextrolimonene.

α -compound, m.p. 93°–94°. Rhombic. $[\alpha]_D = +67.75$. Hydrochloride *lævo*-rotatory.

β -compound, m.p. 110°–111°. Monosymmetric. $[\alpha]_D = -60.48$. Hydrochloride?

Similar results have been obtained by the employment of aniline and benzylamine. The

salts of the bases thus produced possess in every case a rotatory power opposite in direction to that of the base from which each is derived.

From the foregoing statement it is clear that from each of the two active modifications of limonene two distinct series of bases are derived. Two other series may be formed from the inactive hydrocarbon. Thus when the two α -piperidine bases, m.p. 93°–94°, above described, are dissolved in petroleum spirit, and the solutions mixed, an inactive nitrolamine, m.p. 154°, is at once precipitated. A second inactive compound, m.p. 152°, is formed in like manner by mixing the β -limonene bases (Wallach, Annalen, 252, 123).

Limonene oxidised with a weak solution of permanganate gives first a tetrahydric alcohol $C_{10}H_{16}(OH)_4$, m.p. 191.5°–192°, which crystallises in needles and has a faintly sweet taste (G. Wagner, Ber. 23, 2307). By oxidation with nitric or chromic acids limonene yields terpenylic acid (Krafft and Sauer, *ibid.* 1877, 10, 522).

Pure dextrolimonene and *lævo*limonene give when oxidised no toluic or other benzenoid acid, and pure dipentene, which may be obtained from the products of destructive distillation of india-rubber (*v. Caoutchouc*), when oxidised yields the same products as limonene (Chem. Soc. Trans. 53, 879, and 63, 292).

Cis-trans isomerism has been found by Baeyer to exist among the derivatives of dipentene. When the dihydrochloride is produced by the action of hydrogen chloride on eucalyptol at 0°, it forms a camphor-like mass, which melts at 25°. This is assumed to be the *cis*-form, the already known hydrochloride, m.p. 50°, being the *trans*-form. The corresponding hydrobromides have the melting-points 39° and 64° respectively. Both forms yield the same dipentene, but different terpins (*see Terpin*) (Ber. 1894, 26, 2861).

2. Terpinolene. When pinene is mixed with a small quantity of sulphuric or phosphoric acid a considerable evolution of heat is observed, the liquid ultimately becomes optically inactive, and a mixture of hydrocarbons $C_{10}H_{16}$, together with products of polymerisation $(C_{10}H_{16})_n$, results. From the portion which on distillation comes over below 200° may be separated dipentene, terpinolene, and terpinene, together with more or less cymene and small quantities of other compounds. The distillate at about 176°, which was formerly supposed to consist of a single hydrocarbon called 'terpilene,' consists chiefly of dipentene. From the fractions at 180°–190° terpinene and terpinolene may be obtained, though not in a state of purity.

To obtain pure terpinolene γ -terpineol, m.p. 69°–70°, acetate is boiled with quinoline (Baeyer, Ber. 27, 436). Wallach prefers to dissolve terpineol in anhydrous formic acid, whence on the application of gentle heat terpinolene rapidly separates (Annalen, 1909, 368, 1).

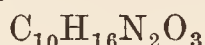
Terpinolene boils at about 185° at atmospheric pressure, at 75° at 14 mm. On account of the readiness with which it undergoes change, these figures cannot be regarded as being exact. By uniting with hydrogen chloride and hydrogen bromide it forms the dipentene compounds, m.p. 50° and m.p. 64°. The nitrosochloride is unknown. It forms an optically inactive tetrabromide, which crystallises in monosymmetric

tables, m.p. 116° , and is quite distinct from the tetrabromides of dipentene and limonene, especially in its instability, the crystals becoming gradually converted into an opaque mass, with lower melting-points 112° *ca.*

3. Terpinene. The product obtained by boiling terpin hydrate with diluted sulphuric acid (Tilden, Chem. Soc. Trans. 33, 250), that formed by the action of slightly diluted sulphuric acid on turpentine (Armstrong and Tilden, *ibid.* 35, 747), also the product of heating the dihydrochloride $C_{10}H_{18}Cl_2$, m.p. 50° , were formerly believed to be identical, and received the name terpinylene or terpinene (Berthelot).

The action of sulphuric or phosphoric acid on terpenes and on terpin is now known to yield, in addition to products of polymerisation (colophene), three distinct hydrocarbons—namely, dipentene, b.p. 175° – 176° , terpinolene already described, b.p. 185° , and terpinene (Wallach).

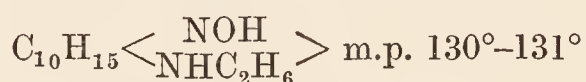
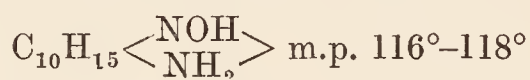
Later researches (Wallach, Annalen, 1908, 362, 285; also 1910, 374, 217) show that the terpinene hitherto obtained is a mixture of two or more isomerides. Ordinary terpinene is believed to contain α -terpinene, boiling at about 179° , β -terpinene, b.p. 173° – 174° , and a γ -terpinene or terpinolene. Ordinary terpinene is characterised by the action of nitrous acid which forms a crystalline nitrosonitrite



m.p. 155° (Wallach, Annalen, 239, 33).

β -Terpinene forms a sparingly soluble crystalline tetrabromide $C_{10}H_{16}Br_4$ [154° – 155°] and a dihydrochloride, m.p. 52° .

Terpinene-nitrosonitrite by the action of bases is converted into nitrolamines, for example :



(Wallach, Annalen, 241, 315).

4. Phellandrene (Pesci, Gazz. chim. ital. 16, 225). The seeds of *Oenanthe phellandrium* (Linn.) contain about 2.5 p.c. of a volatile oil, of which about 80 p.c. consists of a dextro-rotatory terpene, b.p. 171° – 172° . The same hydrocarbon is contained, together with anethol, in the oil of bitter fennel, *Foeniculum vulgare* (Mill.) (Wallach, Annalen, 239, 40). It also forms a constituent of oil of elemi, and in small quantity is said to exist in the oils of cassia, cinnamon (Duyk), and sassafras (Power and Kleber), and in a large number of other essential oils.

In the oil of *Eucalyptus amygdalina* (Labill.) Wallach found the isomeric *l*-phellandrene (Annalen, 246, 232).

Phellandrene in either form is easily alterable by the action of acids into dipentene and terpinene; also into a solid polymeride $C_{20}H_{32}$, m.p. 86° .

Phellandrene is specially characterised by the formation of a nitrosonitrite $C_{10}H_{16} \cdot N_2O_3$, first observed by Cahours, afterwards (Zeits. Chem. 1869, 579) examined by Bunge. Pesci obtained it by the action of a nitrite and dilute sulphuric acid upon the hydrocarbon.

Crude *l*-phellandrene from eucalyptus oil contains two isomeric phellandrenes $C_{10}H_{16}$, together with small quantities of cymene

$C_{10}H_{14}$ and cineole $C_{10}H_{18}O$ (Semmler, Ber. 1903, 36, 1749).

d-Phellandrene from elemi oil is identical with *d*-phellandrene from bitter fennel oil but not with *d*-phellandrene from water fennel oil. The former, which boils at 61° at 11 mm., and has sp.gr. 0.8440 at 19° , and $[\alpha]_D = +61.21^{\circ}$, is to be called *da*-, the latter, which boils at 57° at 11 mm., and has sp.gr. 0.8520 at 20° , and $[\alpha]_D = +18.54^{\circ}$, *d* β -phellandrene. *l*-Phellandrene from eucalyptus is *la*-phellandrene.

Both *da*- and *la*-phellandrene form two nitrites which are separable by crystallisation from acetone and alcohol. The α -nitrite form both melts at 112° – 113° , and has approximately the same rotatory power though in opposite directions and opposite in direction to the rotation of the parent hydrocarbon; thus *d*-phellandrene yields a *l*-nitrite. The β -nitrite from both the phellandrenes melts at 105° , and the rotatory powers of these compounds exhibit similar relations to each other and to the parent. These are the only crystalline and well-characterised derivations of phellandrene.

d β -Phellandrene yields similar derivatives (Wallach, Annalen, 1904, 336, 9); the α -nitrite melts at 102° , the β -nitrite at 97° – 98° .

By reduction of phellandrene nitrite, prepared from water-fennel oil by Pesci's method with zinc and glacial acetic acid, a *la*vo-rotatory diamine is obtained which boils at 250° – 253° . When phellandrene nitrite from eucalyptus is reduced a *la*vo-rotatory diamine $C_{10}H_{16}(NH_2)_2$, which is not identical with Pesci's, is formed also boiling at 250° – 253° . The hydrochloride of this base melts at 209° – 210° . By the distillation it yields cymene, ammonia and ammonium chloride. Phellandrene nitrite treated with ammonia (Pesci), or with sodium ethoxide (Wallach and Herbig), yields a liquid which boils at 134° – 138° , and is identical with the 'nitrophellandrene' described by Pesci (Gazz. chim. ital. 16, 225). Further reduction of the nitrite or of the nitro compound by means of alcohol and sodium leads to the production of tetrahydrocarvone, tetrahydrocarveol, and tetrahydrocarvylamine (Wallach and Herbig, Annalen, 1895, 287, 371).

5. Sylvestrene. Dextrosylvestrene was discovered by Atterberg in Swedish turpentine obtained among the products of destructive distillation of fir-wood (Ber. 10, 1206), also in Russian turpentine oil (Tilden, Chem. Soc. Trans. 33, 80; Wallach, Annalen, 230, 245) in company with *d*-pinene. This variety is dextro-rotatory; $[\alpha]_D = 66.32^{\circ}$. *l*-Sylvestrene has since been found in the oleo-resin of *Dacryodes hexandra* (Griseb.) (More, Chem. Soc. Trans. 1899, 75, 718). Sylvestrene has an odour which is different from that of common turpentine, and resembles that of fresh fir-wood. It has a density at $16^{\circ} = 0.8510$, at $20^{\circ} = 0.8470$, b.p. 175° – 176° . It forms a liquid monohydrochloride and a crystalline dihydrochloride, m.p. 72° , of which $[\alpha]_D = 18.99^{\circ}$, and from which the hydrocarbon may be recovered unchanged by heating with aniline and alcohol. Sylvestrene yields a nitrosochloride $C_{10}H_{16}NOCl$, b.p. 106° – 107° , which is strongly dextro-rotatory, and from which various nitrolamines may be formed. Benzyl-nitrolamine has $[\alpha]_D = 185.6^{\circ}$; m.p. 71° .

Sylvestrene tetrabromide [135°] crystallises in monosymmetric tables (Wallach, *Annalen*, 239, 29). When heated with excess of bromine sylvestrene is converted into *m*-cymene.

Sylvestrene is characterised by the production of a blue colour when a solution of it in acetic anhydride is mixed with a drop of concentrated sulphuric acid, other terpenes giving a red or yellow colour.

Carvestrenes. Dihydrocarvone unites with hydrogen bromide forming an additive compound from which, by the action of alkalis, hydrogen bromide is removed and an isomeride of dihydrocarvone $C_{10}H_{16}O$ is produced to which the name *carone* has been given. This is an oil, b.p. about 210°, and yields a liquid oxime. By reduction of the oxime $C_{10}H_{16}:NOH$ a base *carylamine* $C_{10}H_{19}N$ is produced, and from this by heating the hydrochloride in dilute aqueous or alcoholic solution an isomeric base *vestrylamine* is formed. Vestrylamine hydrochloride yields a hydrocarbon when distilled in a current of hydrogen chloride. The crude hydrocarbon yields together with other products a crystalline hydrobromide $C_{10}H_{16}2HBr$, m.p. 48°–50°. This is *carvestrene hydrobromide*, and by the action of quinoline it yields the hydrocarbon which boils at 178° (corr.). It smells like dipentene, becomes resinous on exposure to the air, decolorises potassium permanganate solution instantaneously, and is oxidised by chromic acid at ordinary temperatures. It is optically inactive, and when mixed with acetic anhydride it gives, on adding sulphuric acid, a blue coloration characteristic of sylvestrene. It bears the same relation to sylvestrene as dipentene to limonene (Baeyer, *Ber.* 1894, 27, 3485).

Carvestrene has more recently been synthesised completely by Perkin and Tattersall (*Chem. Soc. Trans.* 1907, 91, 480).

iso-Carvestrene is also a purely synthetic product (Fisher and Perkin, 1908, 93, 1876). This terpene boils at 176°–177°, has a pungent odour of lemons, and is oxidised but slowly in the air. A drop of sulphuric acid added to its solution in acetic anhydride produces a violet coloration which rapidly fades. No crystalline hydrochloride or hydrobromide or bromide has been obtained.

With the exception of sylvestrene, the terpenes of the *metamenthadiene* series (see below) are not known to occur in essential oils.

6. **Origanene** from *Origanum spp.* grown in Cyprus. A liquid which boils at 160°–164° at 750 mm., with sp.gr. 0.847 at 16°, a rotation of +1.50° in a 1 dm. tube and ref. index $n_D = 1.480$. It forms a nitrosochloride, m.p. 91°–94°, and from this a nitrolbenzylamine, m.p. 104°–105°, and nitrolpiperidide, m.p. 198°, are obtained. The dibromide and hydrobromide are liquid, and a nitrosite has not been obtained. By agitation with dilute sulphuric acid origanene yields ordinary terpin hydrate and the dibromide treated with alcoholic potash yields *p*-cymene. Oxidation by means of hydrogen peroxide yields succinic acid (Pickles, *Chem. Soc. Trans.* 1908, 93, 852).

7. **Crithmene** $C_{10}H_{16}$ has been isolated from the essential oil of *Crithmum maritimum* from Sardinia. It boils at 178°–179°, and yields an α - and a β -nitrosochloride, m.p. 101°–102° and 103°–104° respectively, and a crystalline nitrosite,

m.p. 89°–90°. The dihydrochloride, m.p. 52°, is identical with that of terpinene. Crithmene appears to be a *p*-menthadiene (Francesconi and Sernagiotto, *Atti R. Accad. Lincei*, 1913, [v.] 22, i. 231, 312, 382).

8. **Moslene** $C_{10}H_{16}$ was isolated from the fraction boiling at 173°–175° of the essential oil of *Mosla japonica* (Maxim.), and has also been identified in the terpene fractions of ajowan oil and the oil of *Mosla grosseserrata* (Maxim.). It forms a crystalline nitrosochloride, m.p. 111°, and appears to be a dihydro-*p*-cymene (Murayama, *J. Pharm. Soc. Japan*, 1921, No. 475, 769).

9. **Synthetic menthadienes**. See below (Constitution of the Terpenes).

BICYCLIC TERPENES.

10. α -Pinene.

Australene, or dextro-pinene, of which rectified American turpentine, from *Pinus palustris* (Mill.) and *P. Taeda* (Linn.), and especially the Burmese turpentine from *P. Khasya* (Griff.), almost wholly consists, is obtained by agitating the commercial oil with an alkaline solution, drying completely, and carefully fractionating (156°). Dextro-rotatory $[\alpha]_D = +45.04^\circ$ at 18°. Sp.gr. 0.8765 at 0°/4°, 0.8586 at 25°/25°, 0.8278 at 100°/100° (Tilden, unpublished experiments). This compound is also a constituent of many volatile oils, e.g. Russian and Swedish turpentine oils, from *Pinus sylvestris* (Linn.), and *P. Ledebourii* (Endl.) (Tilden, *Chem. Soc. Trans.* 33, 80); wormwood and spearmint (Brühl, *Ber.* 21, 156), and many others.

Terebenthene or laevopinene. French turpentine oil, from *P. pinaster* (Soland.), consists chiefly of this hydrocarbon. B.p. 156°. $[\alpha]_D = -40.32^\circ$. Sp.gr. 0.8767 at 0°/0°, 0.8619 at 17.88°/17.88° (Riban, *Compt. rend.* 78, 788; 79, 314). Present also in oil of rosemary (Bruylants, *J.* 1879, 944), oil of lemon (Tilden, *Pharm. J.* [3] 9, 654), sage and juniper (*Chem. Soc. Trans.* 31, 554), thyme and anise (Brühl, *Ber.* 21, iii. 156), and others.

By fractional distillation of French turpentine oil α -pinene with the following physical constants was obtained: b.p. 153.5°–154.5° at 760 m.m.; 62° at 32 mm.; sp.gr. 0.8748 at 0°, $n_D^{13} = 1.4690$; $[\alpha]_D^{15} = -43.48^\circ$ (Pariselle, *Compt. rend.* 1921, 172, 1496).

For production and properties of turpentine oils v. OILS, ESSENTIAL.

Both dextro- and laevo-rotatory pinenes from different sources differ considerably in rotatory power, owing to the presence in varying quantities of hydrocarbons of opposite rotatory power. Pure pinene, optically inactive (b.p. 155°–156°, sp.gr. 0.858 at 20°, ref. power $n_D = 1.46553$ at 21°), is obtained by the decomposition of the nitrosochloride by aniline (Wallach, *Annalen*, 253, 243), or better by methylamine or dimethylaniline (Tilden, *Chem. Soc. Trans.* 1904, 763). All varieties of pinene agree in the following chemical characters.

Dry hydrogen chloride unites with the hydrocarbon, forming a monohydrochloride $C_{10}H_{16}HCl$, m.p. 131° (bornyl chloride). If the pinene used is not quite free from moisture a certain amount of dipentene dihydrochloride is formed, and this, with the monohydrochloride

forms a liquid from which the latter can be only partially recovered by fractional distillation or cooling. Pinene obtained by fractional distillation from ordinary turpentine oil contains small quantities of isomeric hydrocarbons (pinolene, β -pinene), which yield liquid hydrochlorides. From such pinene, therefore, the theoretical yield of monohydrochloride is never obtained.

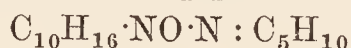
The hydrochloride obtained from dextro-pinene is dextro-rotatory, that from lævopinene is lævo-rotatory. When heated with aniline or with alcoholic potash it yields camphene.

In the presence of water, alcohol, ether, or acetic acid, hydrogen chloride forms a dihydrochloride $C_{10}H_{16}2HCl$, m.p. 50° (*v. Dipentene, infra*).

Nitrosyl chloride gas passed into a solution of the terpene in chloroform at -10° forms a nitrosochloride $C_{10}H_{16}NOCl$ (Tilden, Chem. Soc. Trans. 1875, 514, and 1877, i. 554), the same compound being formed by the action of hydrochloric acid on a cooled mixture of the terpene with amyl or ethyl nitrite and glacial acetic acid (Wallach, Annalen, 245, 245). The best yield of nitrosochloride is obtained when a mixture of dextro- and lævo- pinenes is employed in proportion to provide an optically inactive liquid. When strongly active pinene, dextro- or lævo-, is used the product is small. This appears to be due to the fact that the nitrosochloride is bimolecular $[C_{10}H_{16}NOCl]_2$ (Baeyer, Ber. 1895, 28, 648), and is optically inactive by internal compensation, and when an active variety is used one half of the hydrocarbon or the nitrosochloride undergoes inversion, the change being attended by evolution of heat. The melting-point of the nitrosochloride is usually from 103° to 105° , but after careful recrystallisation from chloroform it is 115° (Tilden, Chem. Soc. Trans. 1904, 85, 759).

The nitrosochloride heated with alcoholic potash yields an isonitroso compound $C_{10}H_{15}NO$, m.p. 132° . (For crystallography see Story-Maskelyne, Chem. Soc. Trans. 1875, 518; and Phil. Mag. 1879, 129.)

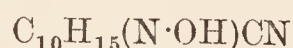
Primary and secondary fatty amines react with the nitrosochloride producing nitrolamines which possess characteristic properties. The nitrolbenzylamine $C_{10}H_{16}NO \cdot NH \cdot CH_2 \cdot C_6H_5$ melts at 122° , and the piperidide



melts at 118° – 119° (Wallach). Alcoholic ammonia converts the nitrosochloride into the nitrolamine $C_{10}H_{16}NO \cdot NH_2$, m.p. 123° – 125° (Leach, Chem. Soc. Trans. 1907, 91, 1).

Pinene nitrosochloride interacts in a different way with aniline and aromatic bases generally. Primary bases give a diazo-compound, while secondary bases yield a nitroso-compound, the hydrocarbon being in both cases regenerated in an optically inactive form.

The nitrosochloride interacts with potassium cyanide in the presence of alcohol, yielding the monomolecular cyanide or nitrile



m.p. 71° (Tilden and Burrows, Chem. Soc. Trans. 1905, 87, 344).

Pinene nitrosochloride also interacts with sodium azide in the presence of alcohol, producing a pinenenitrosoazide $C_{10}H_{15}(N \cdot OH)N_3$ which melts at 120° . When this compound is boiled with water it is converted partly into an

isomeride, melting at 126° , and partly into the oxime of hydroxydihydrocarvone (m.p. 133.5°) already described by Wallach (Forster and Newman, Chem. Soc. Trans. 1911, 99, 244).

Pinene appears to combine with four atoms of bromine, but the product is unstable and quickly evolves hydrogen bromide. If two atomic proportions of bromine are added to a mixture of pinene and carbon tetrachloride a dark liquid is obtained, from which a small quantity of a crystalline dibromide $C_{10}H_{16}Br_2$, m.p. 169° – 170° , can be extracted. When heated with aniline this compound yields ordinary cymene (Wallach, Annalen, 264, 1), and on treatment with zinc-dust and alcohol it yields tricyclene.

Pinene, mixed with alcohol and nitric acid, yields crystallised terpin hydrate, a compound which has long been known as a product of the prolonged contact of turpentine with various aqueous liquids (Wiggers, Annalen, 33, 358; 57, 247; Tilden, Chem. Soc. Trans. 33, 247; Hempel, Annalen, 180, 71; see also *Terpineol, infra*).

When exposed to air or oxygen in the presence of sunlight pinene yields a crystalline compound $C_{10}H_{18}O_2$, discovered by Sobrero (Compt. rend. 33, 66). This is also readily formed by oxidising pinene by means of an aqueous solution of mercuric acetate (Henderson and Agnew, Chem. Soc. Trans. 1909, 95, 289). This compound, sometimes known as *sobrerol*, possesses the properties of a tertiary alcohol. When distilled with dilute acid it loses the elements of water, and yields a compound $C_{10}H_{16}O$, which is identical with one of the products of the action of nitrous acid on pinene, isolated by Wallach and Otto, and called by them *pinole* (Annalen, 253, 249). The alcohol is dextro- or lævo- rotatory according to the character of the terpene from which it is formed. The pure substance melts at 150° , but when equal weights of the two varieties are mixed an inactive compound is obtained, which melts at 131° (Armstrong and Pope, Chem. Soc. Trans. 59, 311). Pinole is an unsaturated compound and yields a crystalline dibromide, m.p. 94° , a hydrochloride and hydrobromide, and a nitrosochloride, m.p. 103° . From the last-named compound a series of nitrolamines have been obtained. By oxidation with permanganate pinole readily yields terpenylic acid $C_8H_{12}O_4$, together with small quantities of other products.

When pinene is oxidised by nitric acid two main products are obtained, namely terebic acid $C_7H_{10}O_4$ and terpenylic acid $C_8H_{12}O_4$. If permanganate is used the chief product is α -pinonic acid $C_{10}H_{16}O_3$ (Baeyer, Ber. 1896, 29, 3). Oxidation with hydrogen peroxide yields as principal products α -terpineol and, in smaller quantity, borneol (Henderson and Sutherland, Trans. Chem. Soc. 1912, 101, 2288). Treatment with dilute hypochlorous acid produces a mixture of three crystalline dichlorohydrins, $C_{10}H_{18}O_2Cl_2$, one of which was proved to be *sobrerol* dichloride, and some tricyclene dichloride $C_{10}H_{16}Cl_2$ (Henderson and Marsh, Trans. 1921, 119, 1492). With chromyl chloride pinene forms an additive compound, $C_{10}H_{16} \cdot 2CrO_2Cl_2$, which when decomposed by water yields a saturated aldehyde, $C_{10}H_{16}O$, an unsaturated ketone, $C_9H_{14}O$, and a product of

the formula $C_{10}H_{15} \cdot OCl$ (Henderson and others, Trans. 1903, 83, 1299; 1908, 93, 288).

Pinene distilled with bleaching powder and water yields a large quantity of chloroform. Picric acid has no action on the pinenes at ordinary temperatures, but at the boiling-point of the hydrocarbon a brisk reaction sets in, and after cooling a pale yellow crystalline compound is deposited, which on boiling with alkali yields borneol (Lextreit, Compt. rend. 102, 555; Tilden and Forster, Chem. Soc. Trans. 1893, 63, 1388).

When heated at 250° – 270° pinene is converted into dipentene, and when boiled with alcoholic sulphuric acid is changed into terpinolene and terpinene.

11. β -Pinene (tropinene) occurs in turpentine oil in small quantity, and may be separated from α -pinene by fractional distillation, b.p. 163° – 164° at 760 mm., 71.5° at 34 mm.; sp.gr. 0.8848 at 0° , $n_D^{13} = 1.479$; $[\alpha]_D^{15} = -19.8^{\circ}$ (Pariselle, Compt. rend., 1921, 172, 1496). It has been obtained, together with fenchene, from *nopinone*, a ketone obtained by Baeyer among the products of oxidation of turpentine oil. Nopinone was prepared and further studied by Wallach and Blumann (Annalen, 1907, 356, 227; Wallach, 1908, 363, 1). The synthetical β -pinene unites with hydrogen chloride to form bornyl chloride [131°] and dipentene dihydrochloride [49° – 50°].

On cautious oxidation it yields β -pinene glycol $C_{10}H_{16}(OH)_2$, m.p. 75° – 77° , and on more vigorous oxidation nopinic acid, $C_{10}H_{16}O_3$, m.p. 126° , and nopinone. The 'nitro-terebenthene,' $C_{10}H_{15}NO_2$, obtained in small quantity by the action of nitrous acid on oil of turpentine was proved by Wallach (Ann., 1906, 346, 243) to be a derivative of β -pinene. On reduction it is converted into 'amino-terebenthene,' a liquid which yields a number of crystalline salts.

Dihydropinene (Pinane), $C_{10}H_{18}$, obtained by passing a mixture of pinene vapour and hydrogen over heated nickel (Sabatier and Senderens, Compt. rend. 1901, 132, 1254) is a liquid with an odour resembling that of camphor, b.p. 166° , sp.gr. 0.862 at 20° . It is a saturated compound, but is attacked fairly easily by nitric acid, and turns brown on exposure to air.

12. Camphene. The monohydrochloride, m.p. 131° (b.p. 210°), of pinene has been long known and was formerly described as 'artificial camphor.' This compound is remarkably stable, but it may be decomposed by heating with sodium stearate or benzoate, with potassium acetate and acetic acid, with alcoholic potash or ammonia, or by a mixture of sodium acetate and caustic soda with alcohol. The resulting hydrocarbon is a camphene, m.p. 51° – 52° , b.p. 160° , dextro- or lævo-rotatory, or inactive, according to the nature of the hydrochloride used and the reagent employed (Berthelot, Compt. rend. 47, 266, and 55, 496, 544). The inactive compound seems to be produced when a high temperature is used. Camphene is also formed from bornyl chloride (art. CAMPHORS, vol. ii. p. 2) by the action of alcoholic potash (Riban), by the action of water and magnesia (Kachler, Annalen, 197, 86), or by heating with aniline to the boiling-point of the latter (Wallach, *ibid.* 230, 234).

Camphene is also formed from camphor chloride (vol. ii. p. 6) and from pinene hydrochloride by the action of sodium (Montgolfier, Compt. rend. 87, 840). In this last case it is accompanied by a hydrocarbon $C_{10}H_{18}$ resembling a paraffin, m.p. 120° , which presents an appearance and odour similar to camphene, but is not attacked by sulphuric or fuming nitric acid. It is best prepared by heating borneol with dilute sulphuric acid (Konowalow, J. Russ. Phys. Chem. Soc. 1905, 340, 40).

Camphene is also formed, together with other products, by the action of strong sulphuric acid on turpentine, and constitutes the chief ingredient in the liquid formerly known as 'terebene' (Armstrong and Tilden, Chem. Soc. Trans. 1879, 745).

Camphene occurs in many essential oils, such as oil of rosemary, spike (*Lavandula spica* [Cav.]), valerian, Siberian fir (*Abies sibirica*), citronella, &c. The melting-point of natural camphene is, however, generally lower than that of the artificial, and Wallach appears to have proved that the derivatives of the camphenes are isomeric, not identical (Annalen, 1907, 367, 72).

Ordinary camphene, active or inactive, possesses a characteristic camphoraceous smell, is soluble in alcohol, and crystallises therefrom in leaflets, m.p. 51° – 52° , b.p. 158.5° – 159.5° . It combines with hydrogen chloride to form a hydrochloride $C_{10}H_{17}Cl$, m.p. 157° , which is distinguished from pinene hydrochloride by its inferior stability (Riban, Compt. rend. 80, 1330; Ehrhardt, Chem. News, 54, 239).

Camphene hydrochloride was formerly regarded as identical with bornyl chloride (Kachler and Spitzer, Annalen, 200, 340), but according to Reychler (Bull. Soc. chim. 1896, [iii.] 15, 366), and later Wagner and Brickner (Ber. 1899, 32, 2302), camphene hydrochloride is identical with *isobornyl* chloride. They regard pinene hydrochloride as the true chloride of borneol. This conclusion is confirmed by Hesse (*ibid.* 1906, 39, 1127).

Camphene in chloroform solution reacts with bromine, with formation of an oily monobromo derivative (b.p. 228°). This compound unites additively with two atoms of bromine to form $C_{10}H_{15}Br_3$, m.p. 77° – 78° . At low temperatures camphene unites with bromine to form a crystalline dibromide $C_{10}H_{16}Br_2$, m.p. 91° , which on distillation with steam is converted into monobromocamphene. Camphene does not combine with nitrosyl chloride. It is converted at about 300° into liquid products which have not been investigated.

When oxidised by chromic acid, ordinary camphene yields camphor, but, according to Marsh and Gardner (Chem. Soc. Trans. 59, 649), when dilute nitric acid is employed as the oxidant a tribasic acid $C_{10}H_{14}O_6$, called by them *camphoic acid*, is produced. Camphoic acid is not produced by the oxidation of camphor or camphoric acid; it has been identified as carboxyl-*apocamphoric acid* by Bredt and Jagelki (Chem. Zeit. 1896, 20, 842).

When ordinary camphene is oxidised by neutral permanganate one of the first products formed is *camphene glycol* $C_{10}H_{16}(OH)_2$, m.p. 200° , together with a ketone, camphenilone $C_9H_{14}O$, m.p. 37° – 38° , and a compound $C_{10}H_{16}O_2$, m.p. 169° – 170° . When acidified the products of

oxidation included camphenecamphoric acid $C_{10}H_{18}O_4$, and camphenylic acid $C_{10}H_{16}O_3$. The origin of some of these products is, however, uncertain (see Wagner, Moycho and Zienkowski, Ber. 1904, 37, 1032, and Moycho and Zienkowski, Annalen, 1905, 340, 17).

Camphene glycol when heated with hydrochloric acid is converted into *camphenilanic aldehyde*, which is readily oxidised to *camphenilanic acid* $C_9H_{15}COOH$, m.p. 65° . This aldehyde is also obtained when the solid compound $C_{10}H_{16} \cdot 2CrO_2Cl_2$, which is produced by the action of chromyl chloride on camphene, is decomposed by water. Camphenilanic acid is transformed into the stereo-isomeric *isocamphenilanic acid*, m.p. 118° , when heated with dilute nitric acid. Camphenylic acid is α -hydroxycamphenilanic acid (Bredt and Jagelki, Ann. 1900, 310, 112).

When oxidised with hydrogen peroxide camphene yields as chief products *camphenanic acid*, m.p. 95° , camphenilone, and isocamphenilanaldehyde, together with smaller quantities of camphene glycol and other products (Henderson and Sutherland, Trans. 1911, 99, 1539).

Hypochlorous acid converts camphene almost quantitatively into camphene chlorohydrin $C_{10}H_{17}OCl$, m.p. 93° , which on treatment with zinc-dust and alcohol is converted into isoborneol, and on oxidation with chromic anhydride yields a chloroketone $C_{10}H_{15}OCl$, m.p. 132° , from which camphor is obtained by heating with zinc-dust and alcohol (Henderson, Heilbron and Howie, Trans. 1914, 115, 1367). Isoborneol $C_{10}H_{17}OH$ is also obtained by heating camphene with acetic acid and dilute sulphuric acid. It crystallises in extremely volatile leaflets, m.p. 212° , in closed tube (Bertram and Wahlbaum, J. pr. Chem. 1899, [2] 49, 1).

Dihydrocamphene $C_{10}H_{18}$, the saturated hydrocarbon obtained by addition of hydrogen to camphene, separates from alcohol in colourless crystals, m.p. 89° .

13. Bornylene was obtained by Wagner and Brickner (Ber. 1900, 33, 2121) by heating bornyl iodide at 170° with concentrated alcoholic potash. It is easily prepared from borneol by conversion of the alcohol into bornyl methyl xanthate $C_{10}H_7O \cdot CS \cdot SCH_3$, and subsequent decomposition of the ester by heating to about 220° (Tschugaeff, J. Russ. Phys. Chem. Soc. 1903, 35, 439). The crude product contains a small quantity of an isomeric terpene, possibly tricyclene, but is readily purified by limited oxidation with hydrogen peroxide (Henderson and Caw, Trans. 1912, 101, 1416). *D*- and *l*-bornylene are thus obtained from *l*- and *d*-borneol respectively.

Bornylene is a colourless crystalline solid, exceptionally volatile, m.p. 113° , b.p. 146° at 745 mm., $[\alpha]_D = -23.94^\circ$ (Bredt, J. pr. Chem. 1911, [2] 84, 778). On oxidation with hydrogen peroxide it yields principally borneol, together with the isomeric epiborneol, camphenanic and isocamphenanic acids, and a mixture of two alcohols of the formula $C_{10}H_{18}O_2$. With chromyl chloride it forms an additive compound $C_{10}H_{16} \cdot 2CrO_2Cl_2$, which on treatment with water yields camphenilanaldehyde (cf. CAMPHENE) and a solid chloroketone, m.p. 165° , which is converted into camphor when heated with concentrated

alcoholic potash at 160° . Bornylene reacts with nitrous acid, yielding a crystalline nitronitrosite, m.p. 163° , and is oxidised by nitric acid to camphoric acid (Henderson and others, Trans. 1913, 103, 1543; 1911, 99, 1887).

Hypochlorous acid converts bornylene into a mixture of (1) a crystalline chlorohydrin $C_{10}H_{17}Cl \cdot OH$, m.p. 99° – 101° , (2) a chlorocamphane $C_{10}H_{17}Cl$, and (3) a dichlorocamphane $C_{10}H_{16}Cl_2$. The latter compounds are also crystalline solids. The chlorohydrin is converted into borneol by treatment with zinc and alcohol, and on oxidation yields the same chlorocamphor as camphene chlorohydrin (Henderson and Mair, Trans. 1923, 123, 1155).

Dihydrobornylene $C_{10}H_{18}$ is obtained by the hydrogenation of bornylene in presence of nickel. It is a crystalline volatile solid, m.p. 153° , b.p. 161° – 162° , is saturated towards potassium permanganate and bromine, and is in fact identical with camphane, which had previously been prepared by the action of sodium and alcohol on bornyl chloride, pinene dibromide and camphene dibromide, and of zinc-dust and hydriodic acid on bornyl iodide (Henderson and Pollock, Trans. 1910, 97, 1620).

14. Sabinene. Oil of savin distilled yields about 30 p.c. of a fraction, boiling between 162° and 170° , which consists principally of the hydrocarbon *sabinene* $C_{10}H_{16}$, b.p. 163° – 165° (sp.gr. 0.84, mol. refr. 44.9, $[\alpha]_D = +80.17^\circ$). This yields an oily dibromide, and when oxidised by cold solution of permanganate it yields a glycol $C_{10}H_{18}O_2$, m.p. 54° . An acid, *sabinenic acid* $C_{10}H_{16}O_3$, m.p. 57° , is formed at the same time: it yields a sparingly soluble sodium salt (Semmler, Ber. 1900, 33, 1455). This is an α -hydroxy acid, losing carbon dioxide when oxidised by lead peroxide, to form sabinene ketone $C_9H_{14}O$, b.p. 218° – 219° , which is *laevo*-rotatory, although sabinene, sabinene glycol and sabinenic acid are all *dextro*-rotatory. Sabinene occurs in the essential oil of Ceylon cardamom and in Majorana oil. When shaken with sulphuric acid sabinene yields a terpin $C_{10}H_{18}(OH)_2$, m.p. 137° , and a terpineol $C_{10}H_{17}OH$, b.p. 209° – 212° , which forms a dihydrochloride $C_{10}H_{18}Cl_2$, m.p. 52° . The same *transterpinene* compound is produced from sabinene by the action of hydrogen chloride in glacial acetic acid. The hydrocarbon is converted into terpinene by boiling dilute sulphuric acid (Wallach, Annalen, 1906, 350, 162).

On oxidation with hydrogen peroxide sabinene yields a mixture of two isomeric glycol anhydrides, $C_{10}H_{16}O(OH)_2$, m.p. 172° and 174° respectively, together with some cymene (Henderson and Robertson, Trans. 1923, 123, 1849).

In the presence of metallic catalysts sabinene takes up two atoms of hydrogen with the formation of the saturated hydrocarbon dihydro-sabinene $C_{10}H_{18}$, b.p. 156° – 157° , sp.gr. 0.8190 at 20° (Wallach, Chem. Zeit. 1911, ii. 1802).

15. Thujene. Several essential oils, such as those of thuja, tansy, wormwood, and sage, contain a ketone $C_{10}H_{16}O$ called thujone or tanacetone. Wallach (Ann. 1904, 336, 247) has shown that this is a mixture of at least two isomeric thujones, α - and β - (tanacetone). The oxime of α -thujone is a liquid, that of β -thujone is a solid; m.p. 54° – 55° . β -Thujone oxime is

converted into the oxime of isothujone, m.p. 119° – 120° , by contact with warm concentrated sulphuric acid. Each of these oximes is reducible to a corresponding base, and the hydrochloride of the base splits under the influence of heat into ammonium chloride and a hydrocarbon $C_{10}H_{16}$.

When β -thujone is reduced with sodium and alcohol it yields thujyl alcohol, b.p. 210° – 212° . By conversion of this alcohol into thujyl methyl xanthate and subsequent distillation of the ester Tschugaeff (Ber. 1904, 37, 1481) obtained α - and β -thujene. The former, which has also been prepared by exhaustive methylation of thujylamine, is a mobile liquid, b.p. 151° – 152.5° , sp.gr. 0.8263 at 20° , $[\alpha]_D = -8.23^{\circ}$. It is exceptionally unstable, resinifies quickly on exposure to air, and is very easily attacked even by dilute acids. It does not yield crystalline derivatives with bromine or with nitrosyl chloride, but gives a characteristic red coloration with acetic anhydride and concentrated sulphuric acid. β -Thujene is a solid, b.p. 150° – 151° , sp.gr. 0.8248 at 20° , $[\alpha]_D = +77.43^{\circ}$.

Reduction of both α - and β -thujene at the ordinary temperature by hydrogen in presence of platinum black leads to the production of thujane $C_{10}H_{18}$, b.p. 157° , sp.gr. 0.8190 at 16° . This hydrocarbon is identical with dihydro-sabinene.

16. Fenchene. Dextrofenchone, $C_{10}H_{16}O$, an isomeride of camphor, is present in fennel oil, and the fraction boiling between 190° and 195° consists chiefly of this compound. Lævofenchone occurs in thuja oil, and is left when the crude ketone is treated with strong nitric acid. By the reduction of *d*-fenchone a lævo-rotatory fenchylic alcohol is obtained. When this is treated with phosphorus pentachloride, and hydrogen chloride is removed from the product by the action of bases, the hydrocarbon fenchene is obtained. It was originally supposed that this terpene was an individual substance. It appears, however, that fenchylic alcohol gives two fenchylic chlorides and these furnish two fenchenes, one dextro-, the other lævo-rotatory. As both are derived from dextrofenchone Wallach distinguishes them as *Dd*-fenchene and *Dl*-fenchene respectively.

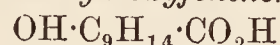
From lævofenchone corresponding *Ld*- and *Ll*-fenchenes have been prepared.

Dl-fenchene has been obtained in a pure state from fenchylamine nitrite (Wallach, Ann. 1896, 362, 181). It has b.p. 155° – 158° , sp.gr. 0.869, $n_D^{19} = 1.4724$, $[\alpha]_D = -32^{\circ}$. It forms a solid dibromide, m.p. 87° – 88° , unites with hydrochloric acid to form fenchyl chloride, and is converted into *Dd*-fenchene when heated with alcoholic sulphuric acid.

According to Komppa and Roschier (J. Soc. Chem. Abstracts, 1917, i. 398, 466; 1918, i. 455; 1919, i. 408) there are five fenchenes. α -, or *Dl*-, fenchene has been obtained from *dla*-fenchocamphorone and from fenchyl chloride. β -, or *Dd*-, fenchene (b.p. 151° – 153° , sp.gr. 0.866 at 20° , $[\alpha]_D = +10.7^{\circ}$) has been obtained from fenchyl alcohol, together with γ - and δ -fenchene. γ -Fenchene, which has also been prepared from *dl* β -fenchocamphorone, together with the β -isomeride, has b.p. 146° – 148° , sp.gr. 0.8539, $n_D^{20} = 1.6063$. γ -Fenchene has a lower

boiling-point than the others, and contains a little cyclofenchene (Aschan's β -pinolene).

The fenchenes yield an unstable liquid dibromide and are distinguished from other terpenes by comparative indifference towards nitric acid. *Dd*-Fenchene is quickly oxidised by a 3 p.c. solution of permanganate, while *Dl*-fenchene is slowly oxidised by the same agent. The product is *hydroxyfenchenic acid*



of which the m.p. and rotation differ according to the origin of the acid.

<i>Dl</i> -Hydroxy-fenchenic acid, m.p. 152° – 153°			
$[\alpha]_D = -56.8^{\circ}$			
<i>Ld</i> -	"	"	m.p. 152° – 153°
$[\alpha]_D = +57.3^{\circ}$			
<i>r</i>	"	"	m.p. 142° – 143°
<i>Dd</i> -	"	"	m.p. 138° – 139°
$[\alpha]_D = +7.69^{\circ}$			

(Wallach and Hertz, Annalen, 1898, 302, 371).

Fenchene has been prepared synthetically from nopinone. The methyl ester of nopinol-acetic acid is obtained by treatment of nopinone with methyl bromoacetate and zinc, and the free acid yields fenchene by loss of carbon dioxide and water (Wallach, Ann. 1897, 363, 3).

17. α -Pinolene. The mixture of liquid hydrochlorides obtained on saturating crude American pinene with hydrogen chloride when decomposed by bases yields a fraction, b.p. 145° – 148° , of constant rotatory power. This is found by Aschan (Ann. 1912, 387, 1) to be a mixture of three isomeric terpenes $C_{10}H_{16}$, (1) bornylene, (2) α -pinolene, and (3) β -pinolene; the two former are oxidised by treatment with permanganate, the last remains unattacked. α -Pinolene, b.p. 144° – 146° , yields a hydrochloride, m.p. 38° . β -Pinolene (cyclofenchene) has b.p. 141.5° – 143.5° , sp.gr. 0.8588 at 20° , $n_D^{20} = 1.44769$, $[\alpha]_D = +0.28^{\circ}$. In dry ether at -15° it forms an unstable crystalline hydrochloride, m.p. 27.5° – 29° . Both hydrochlorides when treated with aniline and alcohol yield *isopinene*, b.p. 154° – 156° , which forms a crystalline hydrochloride, m.p. 36° – 37° . 'Isopinene' appears to be one of the fenchenes.

When α -pinolene is treated with glacial acetic acid and 50 p.c. sulphuric acid, by Bertram and Wahlbaum's method, and the resulting acetate hydrolysed, it yields as chief product *dl*-isofenchyl alcohol, whilst β -pinolene yields a mixture of *dl*-isofenchyl and *dl*-fenchyl alcohols.

18. Dacrydene, from leaves of *Dacrydium Franklini* (Hook.) (Huon Pine of Tasmania) (b.p. 165° – 166° , sp.gr. 0.8524 at 22° , $[\alpha]_D = +14.48^{\circ}$) forms a nitrosochloride, m.p. 120° – 121° , but the bromide is liquid and no solid compound with hydrogen chloride has been obtained (H. G. Smith, The Pines of Australia, Sydney, N.S.W., 1910).

19. A bicyclic terpene has been found among the constituents of Indian turpentine from *Pinus longifolia*, Roxb. It has a characteristic sweet odour and forms a crystalline nitrosite. On oxidation with potassium permanganate it yields dimethylmalonic acid, and under other conditions *transcaronic acid*. This terpene is very probably *d* Δ 3-carene, and is the first

naturally occurring terpene which has been found to contain the carene ring.

20. Tricyclene. Solid pinene dibromide on treatment with zinc-dust and alcohol is converted into a crystalline terpene, *tricyclene*, m.p. 64° – 65° , b.p. 152° . The hydrocarbon has also been prepared from the methyl ester of tricyclenic (dehydrocamphenylic) acid, which on treatment with sodium and alcohol yields the primary alcohol *tricyclol*, m.p. 112° . This alcohol is oxidised to the corresponding aldehyde (b.p. 115° at 31 mm.), and the hydrazone of this aldehyde yields tricyclene when heated to 180° – 195° with an alcoholic solution of sodium ethoxide (Lipp, Ber. 1920, 53, [B] 769). Tricyclene also occurs in ordinary camphene, and remains unattacked when the latter is oxidised with potassium permanganate. It is a relatively stable substance, but is oxidised by potassium permanganate in warm glacial acetic acid solution, yielding *tricyclenic acid* and a carbonyl compound. It is readily converted by sodium hydrogen sulphate at 160° into camphene. Tricyclene dichloride $C_{10}H_{16}Cl_2$, m.p. 176° , is obtained by the action of hypochlorous acid on pinene. It is converted into camphene when heated with sodium in alcoholic solution.

21. β -Pinolene. See α -Pinolene.

Essential oil of Pinus pinea.—According to G. Dupont and M. Barrand (Bull. Soc. chim. 1924, 35, 625) the essential oil of *Pinus pinea*, obtained, in 16–18 p.c. yield, on steam distillation of the turpentine, has $d_{15}^{15} 0.8506$, $a_D = -84.53^{\circ}$, $a_v = -96.02^{\circ}$, $a_1 = -164.12^{\circ}$, $n_D = 1.4700$, $n_v = 1.4707$, $n_1 = 1.4750$. On distillation at 13 mm. through a 2-m. column it yields pinene (16.7 p.c.), *l*-limonene (75.4 p.c.), and an inactive sesquiterpene, $d_{15}^{15} 0.9157$, $n_D^{20} = 1.4983$ (6.6 p.c.). The *l*-limonene ($[a]_D = -123.7^{\circ}$) shows greater optical activity than any natural limonene previously obtained (J. Soc. Chem. Ind. 1924, 43, B. 615).

SESQUITERPENES $C_{15}H_{24}$.

According to Gladstone (Chem. Soc. Trans. 1872, 1), the oils of clove, calamus, cascarilla, patchouli, and cubebs contain a hydrocarbon of this composition. A sesquiterpene has also been found by Wallach (Annalen, 238, 81) in oils of galbanum and savin and in 'huile de cade,' a kind of tar made by distillation of the wood of *Juniperus Oxycedrus* (Linn.). According to the latter chemist, the hydrocarbon *cadinene* obtained from cade or cubebs possesses the following properties. It unites with 2HCl, forming a compound which crystallises from ether in large hemihedral rhombic prisms, m.p. 117° – 118° , the solution of which is lævo-rotatory. Heated with aniline or with sodium acetate the hydrocarbon is set free in a pure state, b.p. 274° – 275° ; sp.gr. 0.921 at $16^{\circ}/16^{\circ}$, $[a]_D = -98.56^{\circ}$. The hydrobromide $C_{15}H_{24} \cdot 2HBr$ melts at 124° – 125° ; the hydriodide $C_{15}H_{24} \cdot 2HI$ at 105° – 106° , with partial decomposition. The hydrocarbon, especially when partially resinified by exposure to the air, gives the following characteristic colour reaction: Dissolved in chloroform or glacial acetic acid, and then shaken up with a few drops of strong sulphuric acid, the liquid assumes an intense green and then blue colour, which when heated passes into red.

Cadinene (lævo-rotatory) also occurs in the oils of betel, camphor, juniper, asafoetida, coto, and olibanum.

Caryophyllene occurs in oils of cloves and copaiba, but has not been obtained pure by fractional distillation. It boils at about 258° – 260° . When dissolved in a mixture of glacial acetic and sulphuric acid and the mixture subsequently steam distilled, a volatile and crystalline alcohol, $C_{15}H_{25}OH$, is formed. The alcohol melts at 96° and boils at 287° – 289° . When treated with dehydrating agents the original hydrocarbon is not reproduced, but an isomeride to which the name *clovene* has been given (Wallach and Walker, Annalen, 271, 285).

Caryophyllene produces liquid addition products with the halogen acids, but it forms a solid nitrosochloride, m.p. 158° – 160° , and nitrosate, m.p. 147° – 150° . The nitrosite forms blue needles, m.p. 107° .

According to Deussen and Lewinsohn (Annalen, 1907, 356, 1) this nitrosochloride is a mixture from which alcoholic ethyl acetate extracts β -caryophyllene nitrosochloride, m.p. 159° , $[a]_D = -98.70^{\circ}$, together with another substance $C_{15}H_{23}O_2N$, m.p. 162.5° – 163.5° , $[a]_D = +217.2^{\circ}$. The residue is the α -nitrosochloride, m.p. 177° – 179° , which is optically inactive and reacts with benzylamine forming the nitrolamine, m.p. 126° – 128° .

Later researches lead to the conclusion that Wallach's caryophyllene is a mixture of two or more isomerides (Deussen, Ber. 1909, 42, 376; Annalen, 1909, 369, 41).

Humulene from oil of hops has been studied by Chapman (Chem. Soc. Trans. 1895, 67, 54, and 780). The sesquiterpene is optically inactive, it boils at 263° – 266° and has a vapour density corresponding to $C_{15}H_{24}$. It forms an oily tetrabromide and yields no alcohol when treated in the same manner as caryophyllene. Humulene forms a liquid dihydrochloride, a white crystalline nitrosochloride, m.p. 164° – 165° , a nitrosate [162° – 163°], and a blue crystalline nitrosite $C_{15}H_{24}N_2O_3$ [*ca.* 121°]. From the nitrosochloride a nitrolpiperidide, m.p. 153° , and nitrolbenzylamine, m.p. 136° , were obtained.

A comparison of caryophyllene and humulene shows that these hydrocarbons are distinct substances (Kremers, Schreiner and James, Pharm. Archives, 1898, i. 209).

Cedrene obtained from oil of cedar is said to boil at 260° (Chapoteaut, Bull. Soc. chim. [ii.] 37, 303). It is lævo-rotatory $a_D = -17^{\circ} 54'$. It produces unstable compounds with bromine and halogen acids, and when oxidised yields with chromic acid a ketone $C_{15}H_{24}O$ (Rousset, *ibid.* 1897, [iii.] 17, 485). According to Semmler and Hofmann the composition of cedrene is $C_{15}H_{22}O$, b.p. 147° – 150° . Cedrene oxidised with permanganate yields cedrene glycol $C_{15}H_{26}O_2$ which crystallises in large prisms, m.p. 160° (Ber. 1907, 40, 3521).

An attempt to prepare from isoprene a polymeride of the composition $C_{15}H_{24}$ proved unsuccessful (Wallach).

Conimene, a hydrocarbon $C_{15}H_{24}$, b.p. 264° , with a pleasant odour, is obtained from the incense-resin (*Protium heptaphyllum* [March]) of British Guiana (Stenhouse and Groves, Chem. Soc. Trans. 1876, i. 175).

POLYTERPENES $C_{20}H_{32}$, &c.

The members of this group may be divided into three classes, viz. (1) Fluid constituents of certain essential oils; (2) products of the polymerisation of terpenes; and (3) caoutchouc and gutta-percha.

1. The least volatile portions of many essential oils contain a hydrocarbon probably having the composition $(C_{10}H_{16})_n$, but very little is known concerning these substances. Some of the oils to which the formula $C_{20}H_{32}$ was formerly attributed appear to be sesquiterpenes, the hydrocarbon from balsam of copaiba for example. See *Caryophyllene*.

2. *Colophene* is a viscid yellow fluid, often strongly fluorescent, which begins to boil at about 300° . It is produced by exposing oil of turpentine or other terpenes to a temperature of about 300° for some hours, or by the action upon them of concentrated sulphuric or phosphoric acid, phosphorus pentoxide, or boron fluoride, &c. The name colophene was given by Deville to the less volatile portion of the product of the action of sulphuric acid on French turpentine, apparently under the impression that it was identical with the oil obtained by distillation of resin. The latter, however, contains oxygen, and exhibits totally different properties.

Colophene obtained by the action of strong sulphuric acid on turpentine oil cannot be distilled without decomposition, even under reduced pressure. The first portions of the distillate contain camphene and dipentene; the boiling-point then rises higher and higher, and even when the temperature approaches that of dull redness a residue is left, which on cooling becomes nearly solid (Armstrong and Tilden, Chem. Soc. Trans. 1879, 748). The portions passing over at 300° and upwards appear to consist of saturated compounds, for they absorb mere traces of hydrogen chloride. Riban has obtained from terebenthene, by the action of antimony trichloride, a solid to which he assigns the formula $C_{40}H_{64}$. This is decomposed by heat, and combines with hydrogen chloride to form two compounds



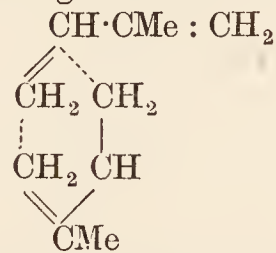
(Compt. rend. 79, 389).

 3. *Caoutchouc*. V. RUBBER.

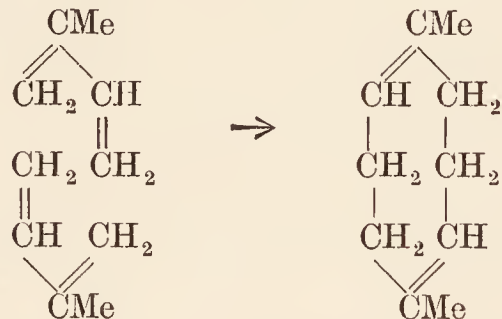
True rubber is a product which results from the coagulation of the milky juice of trees belonging to several distinct natural orders, as explained in the article referred to. It consists, when pure, of a white, exceedingly tough and elastic solid. As usually found in commerce it presents various shades of brown or black colour which are produced by the action of smoke or of atmospheric air on the product of coagulation. Pure india-rubber consists of a hydrocarbon $(C_5H_8)_n$ of high molecular weight, and completely colloidal character. It is insoluble in water and alcohol, but appears to dissolve to a small extent in benzene and its homologues, carbon disulphide, chloroform, and some other liquids forming viscous liquids. The apparent solubility of rubber depends, however, on the treatment to which it has been previously subjected. Rubber unites chemically with many substances, including sulphur and bromine. It combines with the halogen in the proportion of four atoms for every ten atoms of carbon,

and therefore seems to have the same capacity of saturation as the limonenes. When destructively distilled it yields a mixture of hydrocarbons consisting of isoprene (b.p. 36° – 37°), caoutchene which is identical with dipentene (b.p. 176°), and heveene, which appears to be a variety of colophene (b.p. ca. 315°). Rubber, therefore, has the same ultimate composition as the terpenes, and appears to have a formula either $(C_5H_8)_n$ or $(C_{10}H_{16})_n$.

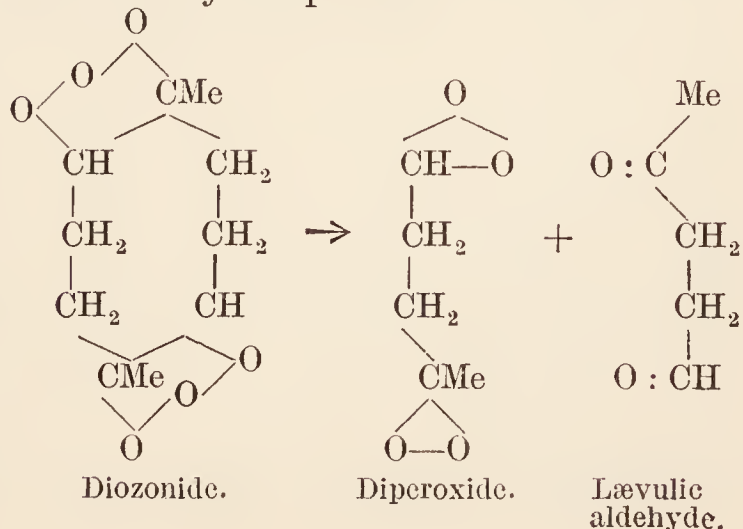
When isoprene is heated to 100° – 200° in contact with a small quantity of acetic acid or is kept in contact with a small quantity of air for a long time, it is converted into rubber. Rubber is also formed by contact of isoprene with metallic sodium (Matthews and Strange, Eng. Pat. 24790 [1910]). When heated alone to a temperature of about 280° isoprene is converted into dipentene. Isoprene having been shown by Mokiewsky (Chem. Zentr. 1899, i. 589) to be β -methyl-divinyl $CH_2:CH.CMe:CH_2$, the condensation into dipentene is easily represented by the following formula, in which two molecules of isoprene are supposed to be united at the points indicated by the dotted lines, the valencies adjusting themselves, but without shifting of the hydrogen atoms—



The conversion of isoprene into caoutchouc is, however, open to several explanations. On the one hand, Harries (Ber. 1905, 38, 3985) assumed the formation of an octadiene as the first product of the union of two molecules of isoprene—



This hypothesis is chiefly based on the fact that when rubber, in chloroform solution, is brought into contact with ozone a compound is formed with two molecules of that substance. This compound has the *molecular* formula $C_{10}H_{16}O_6$. When boiled with water it splits up into lævulic aldehyde or lævulic acid and lævulic aldehyde diperoxide—



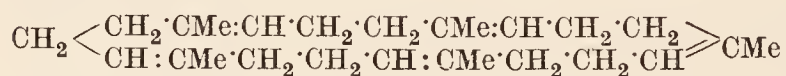
On the other hand, it has been suggested with greater probability that the caoutchouc molecule consists of long chains. One form of hypothesis (Pickles, Chem. Soc. Trans. 1910, 1088) is expressed in the following formula in which an indefinite number of C_5H_8 groups may be linked together—

$CH_2 : CMe \cdot CH : CH_2 + CH_2 : CMe \cdot CH : CH_2, + \&c.$
becoming

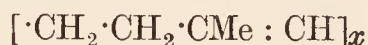
$\dots CH_2 \cdot CMe : CH \cdot CH_2 \cdot CH_2 \cdot CMe : CH \cdot CH_2, \dots \&c.$

The direct conversion of isoprene into rubber with its indefinitely large molecule is in this way easily represented, and it may be remarked that the ready depolymerisation of rubber into isoprene by heat seems to support the view that it is directly resolved into C_5H_8 groups, and not into groups of $C_{10}H_{16}$. The dipentene which accompanies isoprene in the destructive distillation of rubber is probably a secondary product of the polymerisation of isoprene by heat.

One great objection to Harries' formula is the fact that it represents the chemical molecule of rubber as consisting of $C_{10}H_{16}$, whilst it is certain that the actual physical molecule of the colloid is very much more complex, and there seems no way of accounting for the chemical association together of a number of octadiene molecules without loss of free valency, and hence reduction of the saturating power. Further investigations led him (Annalen, 1914, 406, 173) to withdraw the octadiene formula and to replace it by a cyclic structure in which the group $\cdot CH_2 \cdot CH : CMe \cdot CH_2 \cdot$ occurs many times. He suggests the following formula as the most satisfactory representation of the caoutchouc molecule :—



Ostromisslenski (J. Russ. Phys. Chem. Soc. 1915, 47, 1932) also maintains that caoutchouc possesses a unicyclic structure, namely



However, the question of the constitution of caoutchouc cannot yet be regarded as finally settled.

ACTION OF HEAT UPON THE TERPENES.

The terpenes heated to temperatures of 250° – 300° lose their rotatory power and are slowly polymerised (Berthelot, Ann. Chim. [iii.] 39, 5). When ordinary turpentine oil is passed through a tube heated to redness scarcely visible in the dark, it yields a quantity of gas and various liquid products, of which the most important are isoprene C_5H_8 , dipentene $C_{10}H_{16}$, *p*-cymene $C_{10}H_{14}$, and colophene $(C_{10}H_{16})_n$, with relatively small quantities of benzene, toluene, and *m*-xylene (Tilden, Chem. Soc. Trans. 1884, 45, 410). At higher temperatures no isoprene is obtained, but a larger quantity of gas, and the most volatile liquid product is benzene, which is accompanied by some of its homologues, besides naphthalene, anthracene, &c. (Schultz, Ber. 1877, 10, 113).

It has been found by Staudinger and Klever that limonene or dipentene, when diluted with

an indifferent gas, such as nitrogen, or under reduced pressure, yields a much larger quantity of isoprene, amounting to 60 p.c. and upwards. The temperature required is produced by a platinum spiral electrically heated to redness (Ber. 44, 2212). The isoprene thus obtained is said to be purer than the isoprene previously obtained. According to these authors the yield of isoprene under the same circumstances is much smaller when pinene, camphene, terpinene, or terpinolene is employed.

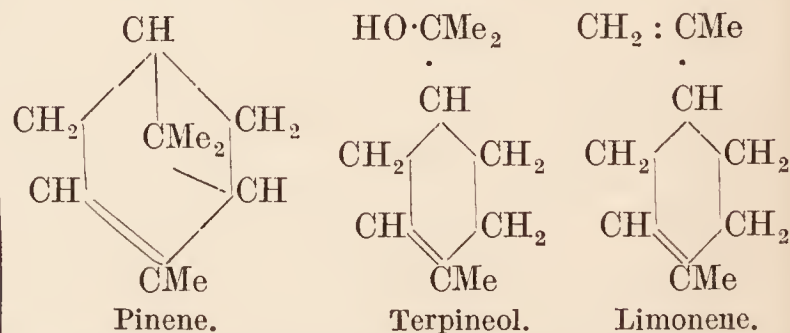
A convenient arrangement of the spiral within a flask connected with a vertical condenser has been described by Harries and Gottlob (Annalen, 1911, 383, 228). The unchanged terpene drops back into the flask, the isoprene passing off into a properly cooled receiver.

Camphene, when heated, yields other products which have not been fully examined.

CONSTITUTION OF THE TERPENES.

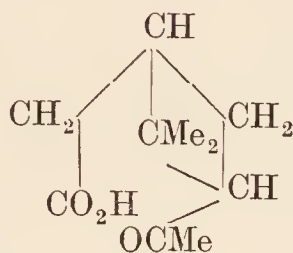
The terpenes generally exhibit many of the properties of olefinic hydrocarbons combining with two or four molecules of bromine, with one or two molecules of hydrogen chloride, and with one or two molecules of water. They also form characteristic compounds with nitrosyl chloride. By the loss of two atoms of hydrogen the terpenes yield a considerable, though varying, amount of common cymene, *methyl-p-isopropyl benzene* (G. Williams, Proc. Roy. Soc. 10, 516; Oppenheim, Ber. 5, 628; Wright, Chem. Soc. Trans. 1873, 686). All the terpenes, when exposed to heat, polymerise into viscous products, and at a temperature of about 400° yield a considerable quantity of isoprene $CH_2 : CH \cdot CMe : CH_2$, a hydrocarbon, which by prolonged heating at a lower temperature is converted into limonene $C_{10}H_{16}$.

Pinene is distinguished by the readiness with which it undergoes isomeric change, especially under the influence of diluted acids, whereby it is converted into terpin, terpineol, and dipentene. The product of its union with hydrogen chloride is, according to conditions, either bornyl chloride $C_{10}H_{17}Cl$ or dipentene dihydrochloride $C_{10}H_{18}Cl_2$, and from neither of these can pinene be regenerated. The only compound from which pinene can be recovered is the nitrosochloride $(C_{10}H_{16}NOCl)_2$, as already mentioned (*v.* Pinene). These facts can be accounted for by the following formulæ which were proposed in 1894 by G. Wagner (Ber. 27, 1636).

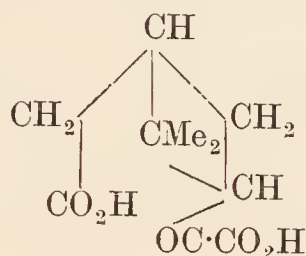


The dimethylated tetramethylene ring in the formula of pinene is very readily broken up by the action of dilute acids, which cause the addition of the elements of water as shown above, yielding terpineol, or the closely connected

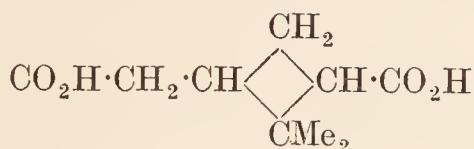
glycol, terpin. It is, however, very stable under the action of neutral or alkaline oxidising agents such as permanganate. This tetramethylene group has been named 'picean' by Baeyer. The products of the oxidation of pinene by permanganate include α -pinonic acid $C_{10}H_{16}O_3$ —



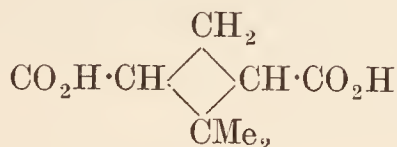
and dibasic pinoyl-formic acid $C_{10}H_{14}O_5$



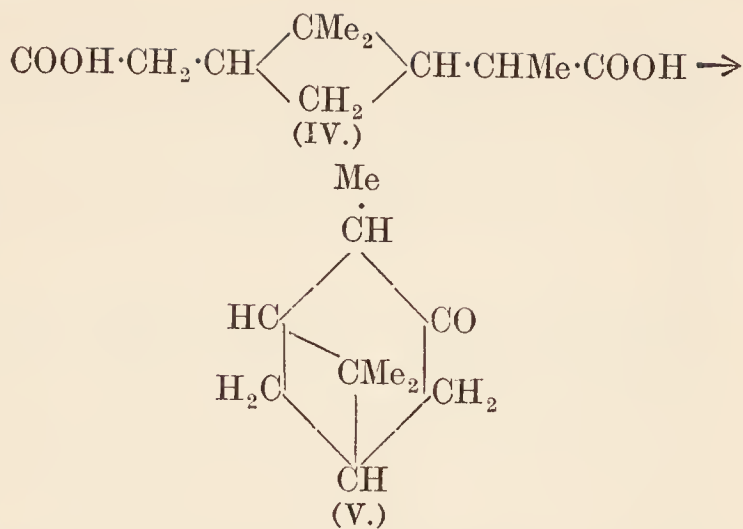
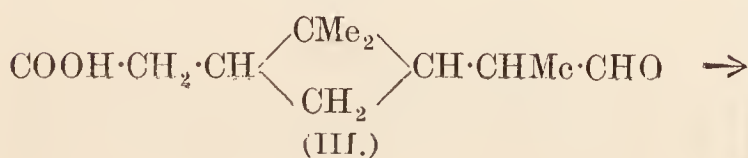
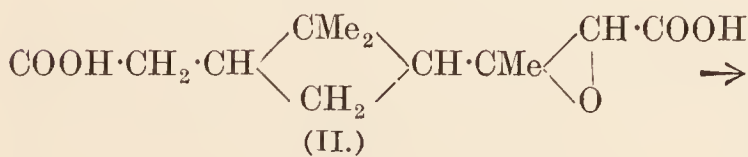
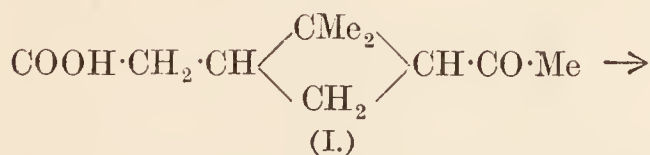
These compounds retain the picean ring which is capable of hydrolytic rupture in both of them, much as in the case of pinene itself. Further oxidation leads to the production from both of these acids of the same pinic acid—



and ultimately of norpinic acid—

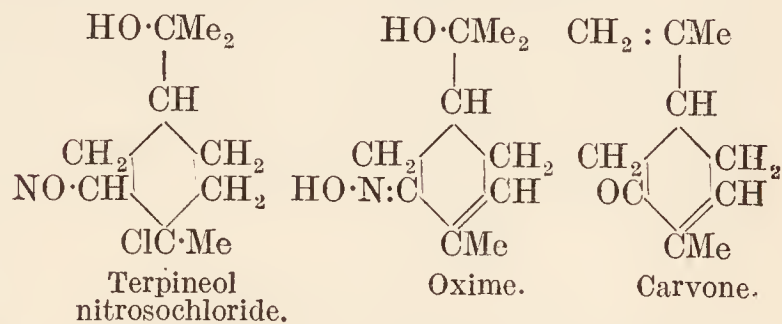


A partial synthesis of pinene from pinonic acid has been effected (Ruzicka and Trebler, *Helv. Chim. Acta*, 1921, 4, 466): ethyl pinonate (I) condenses with ethyl chloroacetate in presence of sodium ethoxide to a glycidic ester, from which the acid (II) is obtained on hydrolysis. On heating at 230° in a vacuum this acid is converted to the semi-aldehyde (III) which is readily oxidised to homopinocamporic acid (IV). Thence pinocamphone (V) is obtainable by applying the Dieckmann reaction, and from the corresponding alcohol, pinocamphol, α -pinene has been obtained by Tschugaeff (*J. Russ. Phys. Chem. Soc.* 1907, 39, 1324) by the xanthate reaction.



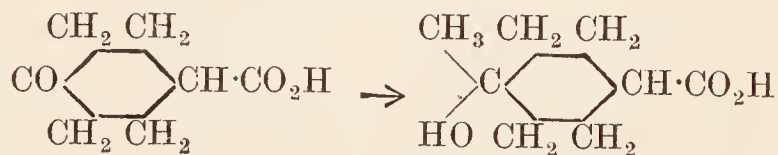
The constitution of limonene was first indicated by the discovery that the nitroso compound $C_{10}H_{15}NO$, obtained from the nitrosochloride $C_{10}H_{16}NOCl$ by the action of alkali, is identical with carvoxime $C_{10}H_{14}:NOH$ (Goldschmidt and Zürer, *Ber.* 18, 2220).

The nitrosochloride of terpineol is also convertible into carvone by removing the elements of hydrogen chloride so as to produce the oxime of the hydroxy ketone from which carvone is obtained by the action of acids (Wallach).

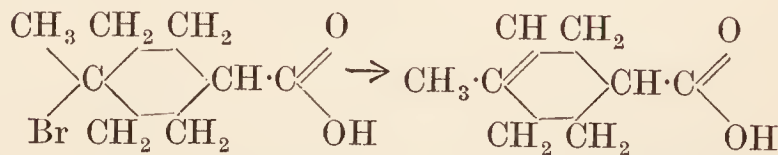


More recently the formulæ of terpineol and limonene have been completely established by synthesis, the principal steps in the process being the following:—

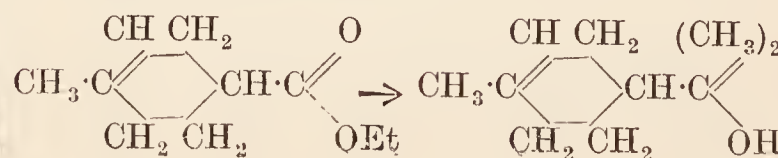
The esters of β -iodopropionic acid and sodiocyanacetic acid are brought together and after interaction the product is hydrolysed. Pentane- $\alpha\gamma\epsilon$ -tricarboxylic ester is thus obtained from which δ -ketohexhydrobenzoic acid is formed by treatment with acetic anhydride and distillation. The ester of this acid in contact with magnesium methyl iodide yields δ -hydroxyhexahydro-*p*-toluic acid—



Hydrogen bromide converts this toluic acid into the corresponding bromo derivative, which, when treated with weak alkalis or pyridine, loses hydrogen bromide and yields Δ^1 -tetrahydro-*p*-toluic acid—



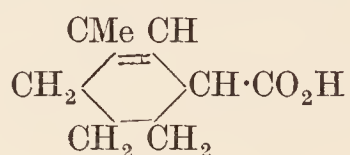
The ester of this unsaturated acid is converted by magnesium methyl iodide in ethereal solution into inactive *terpineol*—



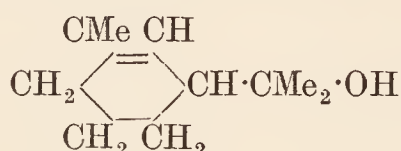
By the simple abstraction of water from terpineol by means of potassium hydrogen sulphate dipentene results, and hence the position of the second ethylenic bond in that compound is determined. These formulæ are identical with those proposed by Wagner (W. H. Perkin, junr., Chem. Soc. Trans. 1904, 654).

Optically active *d*- and *l*-terpineols were afterwards prepared by Perkin and Fisher (*ibid.* 1908, 1871).

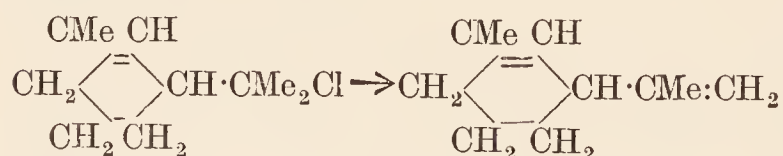
The great majority of the terpenes found in nature are compounds in which the side chains occupy the *para*- position as in limonene. The sylvestrene (*q.v.*) discovered by Atterberg in Swedish turpentine has, however, been shown by Perkin to be a *meta*- compound. Proceeding from Δ^1 -tetrahydro-*m*-toluic acid—



a dextro-rotatory hydrocarbon identical with natural sylvestrene has been built up by synthesis. The *d*-acid was first isolated from the inactive mixture by means of brucine and the ester was made to interact with magnesium methyl iodide. The resulting *d*-dihydrocarvestrenol is the representative of terpineol in the *meta* series and is represented by the following formula—

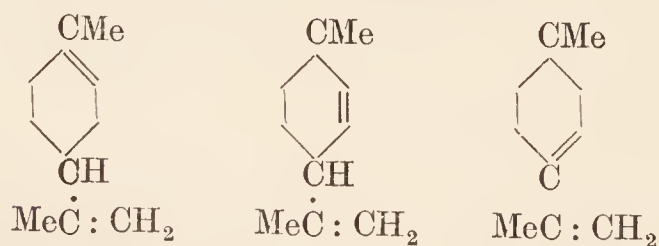


By the action of hydrogen chloride it yields *d*-carvestrene dihydrochloride which melts at 72° and is identical with the hydrochloride obtained from natural sylvestrene. The hydrocarbon is isolated from the hydrochloride by heating it with aniline—

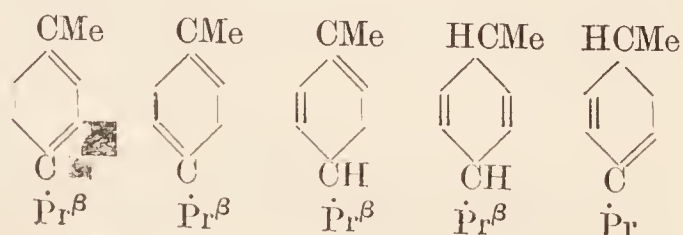


(Perkin, Chem. Soc. Proc. 1910, 97).

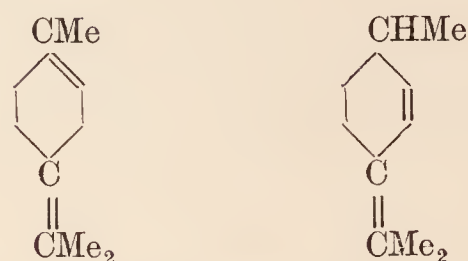
It is now apparent that the formulæ of some of the other natural terpenes are probably closely related to the formula of limonene. Thus there may be theoretically three compounds containing $\cdot\text{Me}$ and $\text{CMe} : \text{CH}_2$ in the *para*- position, while there is one double bond in the ring—



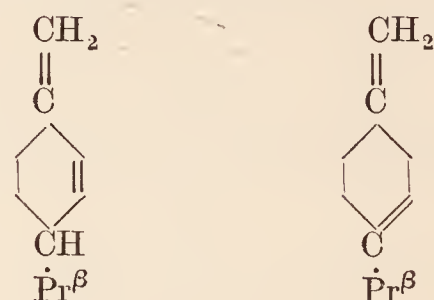
There may also be five isomeric dihydrocymenes—



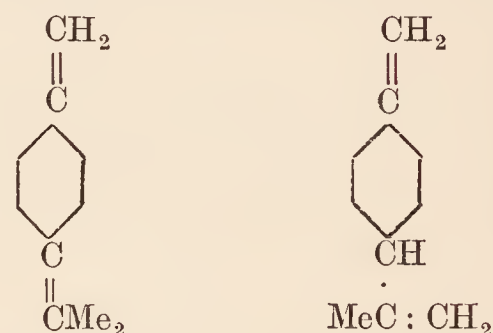
There may be two other isomerides of the type—



Two more of the following form :—

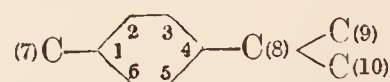


And lastly two isomerides in which the double linking is wholly external to the ring—



Of some of these there are also geometrical isomeric forms.

It is sometimes convenient to adopt a system of numbering the carbon atoms as introduced by Baeyer in the case of the terpenes. The *para*- series is based on the formula of hexahydrocymene—



According to this system dipentene, for example, is $\Delta^{1.8(9)}$ -*p*-menthadiene and terpineol is $\Delta^{1.8}$ -*p*-menthenol 8.

The hydrocarbons enumerated above are only the varieties in which the *para*- position is assumed by the side chains, but these and others already known may be arranged under the following divisions.

MENTHADIENES $\text{C}_{10}\text{H}_{16}$.

I. Derivatives of cyclohexene—

1. *Para*-. Limonene and dipentene, terpinene, phellandrene.
2. *Meta*-. Sylvestrene.
3. *Ortho*-. Synthetical products unknown to occur as natural products.

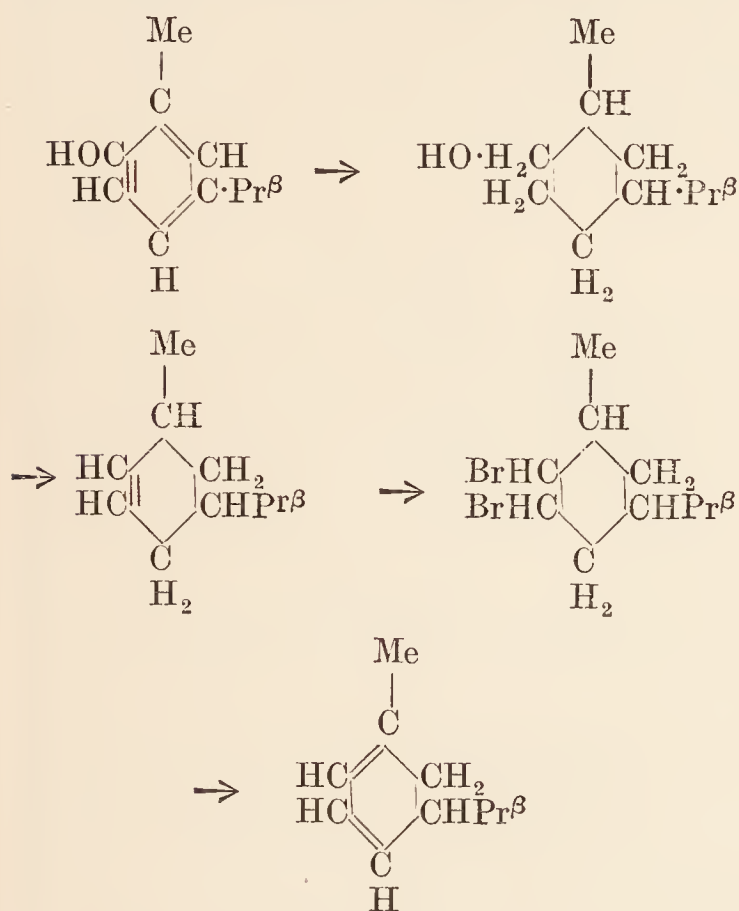
II. Derivatives of cyclohexene with bridged rings—

1. *Para*- containing two pentamethylene rings: fenchene, camphene, bornylene.
2. *Meta*- containing one tetramethylene ring: pinene.
3. *Meta*- containing one trimethylene ring: sabinene, thujene.

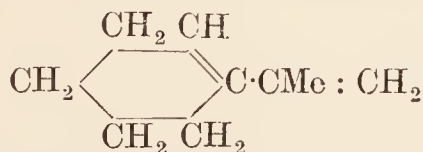
III. Tricyclic terpenes: Tricyclene, cyclofenchene.

No representative of the *o*-menthadienes has yet been discovered in natural essential oils, but five of the six possible isomers, together with the corresponding menthenols, have now been prepared synthetically by Perkin and his collaborators by methods which resemble in general those used for the synthesis of the compounds of the *p*-series (Trans. 1911, 99, 118, 518, 526, 727, 741).

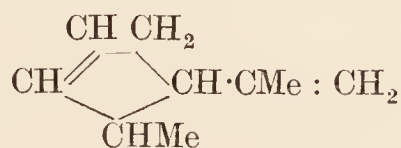
Menthadienes of the *para*- and *meta*- series have also been synthesised by Henderson and others (Trans. 1911, 99, 2159; 1912, 101, 2563; 1920, 117, 144) by methods which may be illustrated as follows: 6-Hydroxy-*m*-isocymene is converted into *m*-menthanol-6 by hydrogenation in presence of nickel. Dehydration of the menthanol by heating with oxalic acid yields a *m*-menthene $C_{10}H_{18}$, which unites with bromine to form a dibromide. From the dibromide the *m*-menthadiene is obtained by heating with alcoholic potash.



Perkin has also made progress in the synthesis of lower homologues of the terpenes. The hydrocarbons C_9H_{14} prepared belong to two types. One of these is derived from cyclohexane containing no methyl group in the ring (Matsubara and Perkin, *ibid.* 1905, 661).

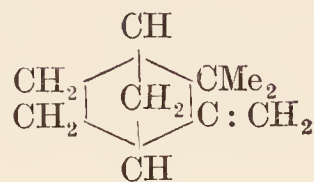


The other is framed on a cyclopentene containing a methyl group (Haworth and Perkin, *ibid.* 1908, 573).

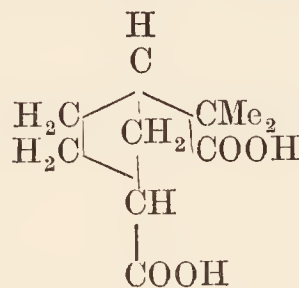


The constitution of the solid terpene, camphene, has been a subject of discussion, but the

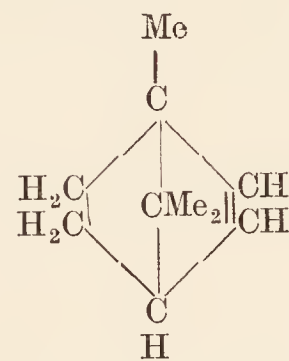
formula assigned to it long ago by Wagner, namely—



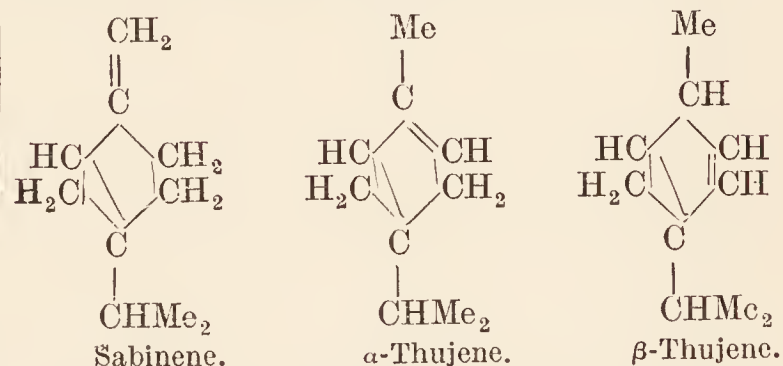
(Ber. 1900, 33, 2121) is now generally accepted. The correctness of Wagner's formula has been almost definitely established by Lipp's (Ber. 1914, 47, 871) synthesis of camphenic acid



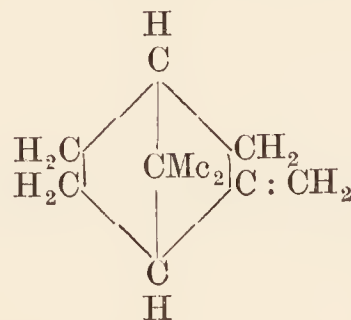
The preparation of bornylene from borneol, and its oxidation to camphoric acid, lead to the conclusion that its constitution must be represented by the formula—



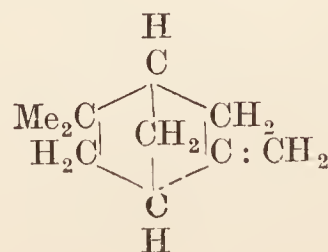
The following formulæ are ascribed to sabinene and the thujenes respectively:—



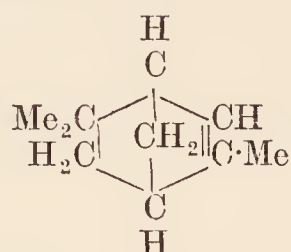
Roschier, by application of the method of ozonisation, concludes (J. Chem. Soc. Abs. 1919, i. 408) that the formula of α -fenchene is



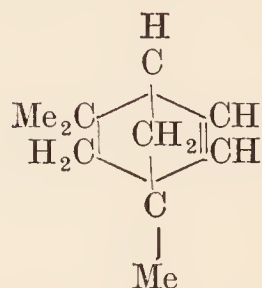
and that of β -fenchene



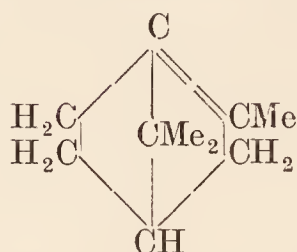
The fenchene of b.p. 145° – 147° is probably



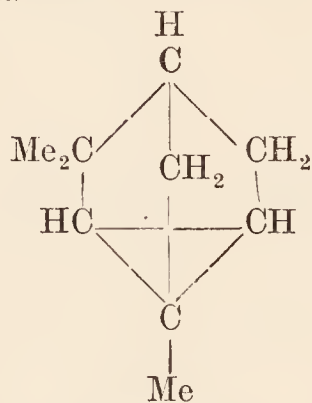
whilst the fenchene of lowest boiling-point is probably



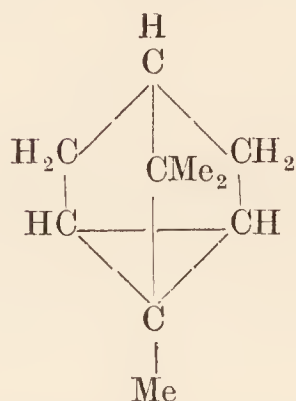
The formula of α -pinolene is probably



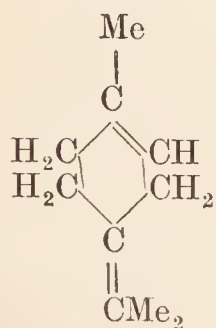
Cyclofenchene (β -pinolene) is represented by the formula



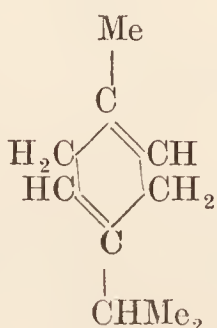
and tricyclene by the formula



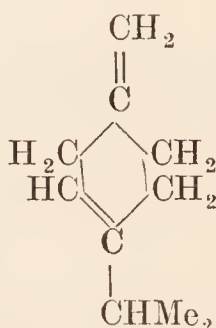
The following formulæ are assigned to the other monocyclic terpenes (*cf.* Wallach, *Terpene und Campher*) :—



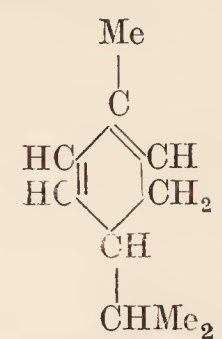
Terpinolene.



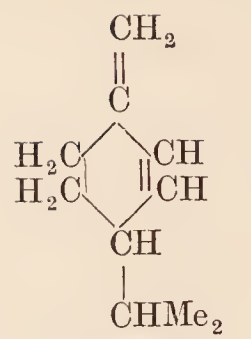
α -Terpinene.



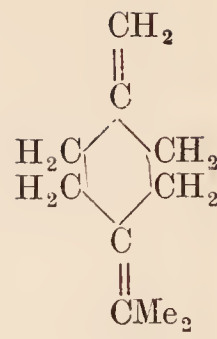
β -Terpinene.



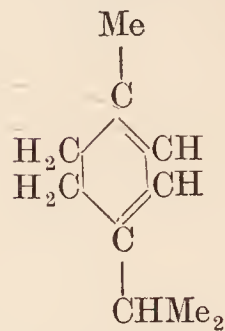
α -Phellandrene.



β -Phellandrene.



Crithmene.



Origanene.

For the optical properties of the terpenes, such as specific rotatory power and especially refractivity, and their relation to the constitution of the hydrocarbons, a useful summary will be found in Smiles' *Relations between Chemical Constitution and Physical Properties* (Longmans' Text-books of Physical Chemistry).

OXIDISED COMPOUNDS RELATED TO THE TERPENES.

1. **Absinthol** $C_{10}H_{16}O$, identical with thujone.
 2. **Borneol** $C_{10}H_{17}OH$, *v. vol. ii.*, CAMPHORS.
 3. **Cajeputol** $C_{10}H_{18}O$, identical with cineol.
 4. **Carveol** $C_{10}H_{16}O$, *v. vol. ii.*, CAMPHORS.
 5. **Carvone** $C_{10}H_{14}O$, *v. vol. iii.*, KETONES.
 6. **Camphor** $C_{10}H_{16}O$, *v. vol. i.*
 7. **Cineol** $C_{10}H_{18}O$, *v. vol. ii.*, CAMPHORS; SANTONICA.
 8. **Citronellol** $C_{10}H_{19}OH$, an alcohol similar to geraniol found in citronella and rose oils.
 9. **Coriandrol** $C_{10}H_{17}OH$, identical with *d*-linalool.
 10. **Eucalyptol** $C_{10}H_{18}O$, identical with cineol.
 11. **Fenchone** $C_{10}H_{16}O$, *v. vol. iii.*, KETONES.
 12. **Geraniol** $C_{10}H_{17}OH$. Indian oil of geranium (*Andropogon Schœnanthus* [Linn.]) consists chiefly of this compound (Semmler, *Ber.* 23, 1098, 2965, 3556; 24, 682).
- Geraniol is an optically inactive compound with a smell of roses. It boils at 229° – 230° . When oxidised by chromic acid it yields the corresponding aldehyde, citral or geranaldehyde $C_{10}H_{16}O$. Further oxidation yield geranic acid $C_{10}H_{16}O_2$, which is monobasic. Geraniol heated with potassium hydrogen sulphate yields a terpene, geraniene, which boils at 172° – 176° .

13. **Citral**, the aldehyde, occurs as a natural constituent of the oil of lemon, lemon grass, and many other essential oils. It boils at 228° – 229° under ordinary pressure, and is optically inactive. It unites with four atoms of bromine, and is characterised by the readiness with which by the action of potassium hydrogen sulphate it yields ordinary cymene. In other respects it gives the usual reactions of aldehydes. It reduces silver solutions, combines to form a crystalline compound with sodium hydrogen sulphite, and reproduces the colour of rosaniline from a sulphite solution.

It also yields an aldoxime and a semi-carbazone.

Citral, purified by a modification of Tiemann's method (A. 1899, i. 622), was condensed with acetone by means of sodium ethoxide, giving a 55 p.c. yield of pure ψ -ionone. The best condensing agent for converting ψ -ionone into α -ionone was found to be 85 p.c. phosphoric acid. ψ -Ethylionone, prepared from citral and methyl propyl ketone, is a pale yellow oil, b.p. 155°–158°/8 mm.; its structure is probably $\text{Me}_2\text{C} : \text{CH} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CMe} : \text{CH} \cdot \text{CH} : \text{CH} \cdot \text{CO} \cdot \text{Pr}$. It is converted by means of 85 p.c. phosphoric acid into ethylionone, a pale yellow oil, b.p. 138°–140°/8 mm., possessing a pleasant odour of violets.

Citral condenses with acetophenone, in presence of sodium ethoxide, to form phenyl ψ -ionone, an odourless, viscous, pale yellow oil, b.p. 182°–185°/4 mm. Phenylionone, prepared from it by the action of 85 p.c. phosphoric acid, is a pale yellow, viscous oil, b.p. 172°–175°/4.5 mm., with a very faint but rather disagreeable odour, the violet fragrance being almost entirely suppressed.

Attempts to condense citral with diethyl ketone or dipropyl ketone were unsuccessful (H. Hibbert and L. T. Cannon, J. Amer. Chem. Soc. 1924, 46, 119; Chem. Soc. Abstr. 1924, 126, i. 262).

Geranic acid, which is best formed from the nitrile by boiling with potash, is a colourless oil possessing an odour like that of the higher fatty acids. When distilled under ordinary pressure it yields carbon dioxide and a hydrocarbon, geraniolene C_9H_{16} , which boils at 142°–143°. Geraniolene forms a liquid tetrabromide $\text{C}_9\text{H}_{16}\text{Br}_4$.

14. **Linalool** $\text{C}_{10}\text{H}_{17}\cdot\text{OH}$. This substance is very widely distributed in essential oils derived from various plants. The name has reference to the wood of the lignum aloes (*Aquilaria Agallocha* [Roxb.]), in which it was originally recognised, but the alcohol or its acetate is found in the oils of lavender, bergamot, petit grain (leaves and shoots of orange), neroli, &c. It is distinguished from geraniol, with which it is isomeric, by its lower boiling-point and by its lævo-rotatory action on the polarised ray. The boiling-point under atmospheric pressure is about 198°–199°.

Linalool treated with acetic anhydride yields, at the ordinary temperature, an acetate which regenerates linalool on saponification, but if the acetate is heated to 100° and upwards it undergoes isomeric change, and on saponification it yields geraniol (Bouchardat, Compt. rend. 116, 1253).

d- or l-Linalool and geraniol, shaken with dilute sulphuric acid, are converted almost quantitatively into terpin hydrate (Tiemann and Schmidt, Ber. 1895, 28, 2137).

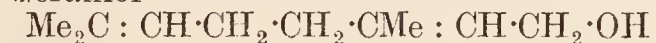
Linalool on oxidation by means of acid reagents yields citral, the aldehyde of geraniol.

The following constitution is assigned to these compounds (Tiemann and Semmler, Ber. 1895, 28, 2126).

Linalool



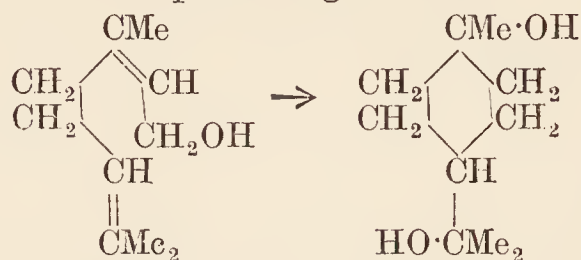
Geraniol



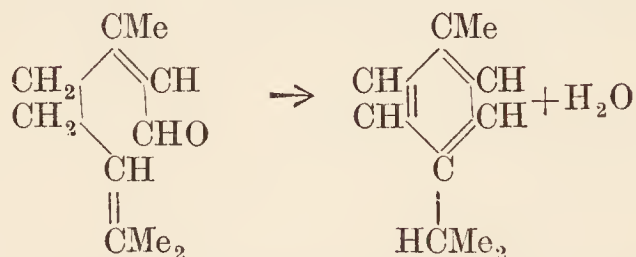
Citral



These open chain compounds are, however, readily converted into cyclic compounds, especially by the action of acids, for example, in the production of terpin from geraniol—



and in the production of cymene from citral.



15. **Coriandrol** is dextro-rotatory linalool (Semmler, Ber. 24, 206; Tiemann and Semmler, *ibid.* 26, 2713).

16. **Menthol** $\text{C}_{10}\text{H}_{19}\text{OH}$, v. vol. ii., CAMPHORS.

17. **Pinole** $\text{C}_{10}\text{H}_{16}\text{O}$, see under *Pinene*.

18. **Pulegone** $\text{C}_{10}\text{H}_{16}\text{O}$, v. vol. iii., KETONES.

19. **Sobrerol** $\text{C}_{10}\text{H}_{18}\text{O}_2$, see under *Pinene*.

20. **Sobrerone** $\text{C}_{10}\text{H}_{16}\text{O}$, identical with pinole.

21. **Tanacetone** $\text{C}_{10}\text{H}_{16}\text{O}$, v. vol. iii., KETONES.

22. **Terpineol** $\text{C}_{10}\text{H}_{17}\text{OH}$. *Terpinol* was the name given by List (Annalen, 1848, 67, 362) to the liquid obtained by the action of dilute acids upon terpin hydrate.

When crystallised terpin is boiled with water and a small quantity, say 1 p.c., of hydrochloric acid is added, the crystals disappear and a turbid fluid results, from which by distillation an oily liquid, lighter than water and possessing a peculiar fragrant odour, resembling that of lilac, is obtained. When the oil is dried and distilled, the whole comes over, with the exception of a few drops at first, between 205° and 215°. Treated with sodium, terpineol dissolves one atom of the metal; and by contact with excess of hydrochloric acid it becomes coloured deep purple, but the colour disappears and the whole is converted into dipentene hydrochloride $\text{C}_{10}\text{H}_{18}\text{Cl}_2$ (m.p. 50°); when mixed gradually with a nearly equal volume of sulphuric acid diluted with half its bulk of water, very little heat is evolved, but solution is complete, and on adding to the mixture three or four volumes of water a mass of crystallised terpin hydrate is obtained. Terpineol is also quickly converted into terpin hydrate by a mixture of nitric acid and alcohol (Tilden. Chem. Soc. Trans. 1878, 247; 1879, 287). Terpineol absorbs two atoms of bromine (Tilden, *ibid.* 1888, 882), and it is, therefore, an unsaturated tertiary alcohol $\text{C}_{10}\text{H}_{17}(\text{OH})$, of which the corresponding glycol is terpin $\text{C}_{10}\text{H}_{18}(\text{OH})_2$. By boiling with potassium hydrogen sulphate terpineol splits into water and dipentene.

Terpincol yields a nitrosochloride



from which a piperidine [m.p. 159°–160°] and anilide [m.p. 155°–156°] are obtainable (Wallach and Kerckhoff, Annalen, 1893, 275, 103).

More recent researches have shown that liquid terpincol obtained as described or by hydrolysis of the corresponding acetate contains

two distinct compounds. Bouchardat and Voiry (Compt. rend. 1887, 104, 996) were the first to obtain crystals by cooling. The m.p. was found to be 35° (Wallach). Distilled under reduced pressure liquid terpineol yields two principal fractions, boiling at 212°–215° and 218°–220° at ordinary pressure. Both solidify on cooling, the former having the m.p. 32°–33°, and the latter 35°–36°.

The terpineol [m.p. 35°–36°] forms a nitrosochloride [m.p. 122°], which yields the piperidide mentioned above [m.p. 159°–160°]. Its phenylurethane $\text{NHC}_6\text{H}_5\cdot\text{CO}\cdot\text{OC}_{10}\text{H}_{17}$ melts at 112°–113°. The new terpineol [m.p. 32°–33°] gives a nitrosochloride [m.p. 102°–103°], but does not readily yield a piperidide. The phenylurethane melts at 85°.

Both these terpineols have been produced synthetically by W. H. Perkin (Chem. Soc. Trans. 1904, 85, 654), starting from ethyl β -iodopropionate and ethylsodiocynoacetate. Their constitution is therefore now fully established.

These compounds are optically inactive, but active terpineols have been obtained from other sources. *l*-Linalool $\text{C}_{10}\text{H}_{18}\text{O}$, when heated with acetic acid containing a small quantity of sulphuric acid yields *d*-terpineol, together with geraniol, while in similar way *d*-linalool yields *l*-terpineol (Stephan, J. pr. Chem. 1898, [ii.] 58, 109).

Optically active terpineols have been produced synthetically by Perkin and Fisher (Chem. Soc. Trans. 1908, 93, 1871) by resolving the corresponding *dl*-cyclohexene carboxylic acid by means of brucine or strychnine.

Active terpineols also occur in certain essential oils, *e.g.* oil of *Asarum canadense* [Linn.] (Power and Lees, *ibid.* 1902, 81, 63).

23. Terpin $\text{C}_{10}\text{H}_{18}(\text{OH})_2$ and **Terpin hydrate** $\text{C}_{10}\text{H}_{18}(\text{OH})_2\cdot\text{H}_2\text{O}$. This compound is occasionally found in old samples of turpentine oil containing a little water, and in furniture polish of which turpentine is an ingredient. It is easily obtained by the action of a mixture of nitric acid and alcohol upon turpentine oil (Wiggers, Annalen, 1846, 57, 251). Hempel recommends (*ibid.* 180, 71) 4 parts oil of turpentine to 1 part of alcohol and 1 part of nitric acid. In any case, the mixture is shaken up at intervals until in the course of about two days the smell of turpentine has disappeared. The liquid is then poured out into shallow dishes, a little alcohol being added occasionally as long as crystals are deposited (Tilden, Chem. Soc. Trans. 33, 247). No crystals are formed under the same circumstances from the limonenes, but from the hydrochlorides of these hydrocarbons terpineol, and hence terpin is easily obtained by the action of water or dilute alcohol.

Terpin hydrate [116°–117°] dissolves in about 200 parts of cold, and in 22 parts of boiling, water. It is easily soluble in alcohol, but not in petroleum. It is optically inactive, and is chemically saturated. Anhydrous terpin melts at 104°–105°, and boils at 258°. The crystals have been examined by List (Annalen, 67, 362), by Rammelsberg (Poggendorff's Annalen, 63, 570), and by Maskelyne (Phil. Mag. 1879, 132).

Exposed to hydrogen chloride the crystals deliquesce, become purple, and finally give a mass of the colourless dipentene dichloride $\text{C}_{10}\text{H}_{18}\text{Cl}_2$ [m.p. 50°]. Boiled with water slightly

acidified with hydrochloric or sulphuric acid it yields terpineol. Boiled with moderately strong sulphuric acid it yields a mixture of dipentene, terpinene, and terpinolene.

Cis- and *trans*- terpins have been obtained by Baeyer from the corresponding *cis*- and *trans*-hydrobromides of dipentene (Ber. 1894, 26, 2861). *Cis*dihydrobromide when treated successively with silver acetate and alcoholic potash gives ordinary terpin. The *trans*-dihydrobromide, when similarly treated, yields the *trans*-terpin which crystallises without water, melts at 156°–158°, and boils at 263°–265°.

Terpin, when passed over alumina in glass at 310°–320°, yields terpinolene; terpineol yields a liquid, presumably terpinolene. The catalyst remains active for several days, and is easily regenerated by heat. Terpinolene passed over copper turnings at 500°–550° gave a gas containing 27 p.c. C_nH_{2n} , 15 p.c. $\text{C}_n\text{H}_{2n+2}$, 18 p.c. CH_4 , 40 p.c. H_2 , and a liquid containing benzene, cyclohexane, toluene, methylcyclohexane, *m*-xylene, and *m*-cymene (Mailhe, J. Usines Gaz. 1923, 47, 370; Chem. Soc. Abstr. 1924, 126, i. 865).

24. Thujone $\text{C}_{10}\text{H}_{16}\text{O}$, α - and β -, the latter identical with tanacetone.

W. A. T., revised by G. G. H.

TERPENYLIC ACID *v.* LACTONES.

Tiemann and his collaborators (Chem. Soc. Abstr. 1895, i. 548; 1896, i. 385; 1897, i. 84) have suggested that methoethylheptanonolide yields terpenylic acid on oxidation by chromic acid, and terebic acid when oxidised by nitric acid, and may be used as a source of these two acids. Locquin (Bull. Soc. chim. 1913, [iv.] 13, 166) finds that on oxidation by nitric acid, terpenylic acid is the chief product (58.2 p.c. of the theoretical), the yield of terebic acid (18.6 p.c. of the theoretical) being small. The preparation and separation of the two acids are described (Chem. Soc. Abstr. 1913, i. 341).

TERRA ALBA *v.* GYPSUM.

TERRA CATECHU. Syn. with CATECHU (*q.v.*).

TERRA CHE BRUCIA or *Val d'Arno Superiore Resin v. RESINS.*

TERRA DI SIENNA. *Raw Sienna v. PIGMENTS.*

TERRA FOLIATA TARTARI. Potassium acetate.

TERRA JAPONICA. Syn. with CATECHU (*q.v.*)

TERRA LEMNIA v. LEMNIAN EARTH.

TERRA MIRACULOSA. An old name for bole (*q.v.*).

TERRA MURIATICA. An obsolete name for magnesia.

TERRA PONDEROSA. An old name for baryta (*q.v.*).

TERRA UMBRA. Umber (*q.v.*).

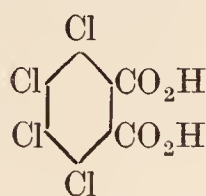
TESTADEN v. SYNTHETIC DRUGS.

TETHELIN v. PITUITARY BODY.

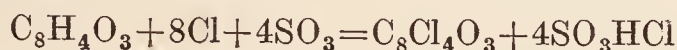
TETRACHLOROBENZALDEHYDE is obtained by passing chlorine through toluene at ordinary temperatures in presence of ferric chloride, when trichlorotoluene separates out. This is again treated with chlorine eventually at 100°–130° in presence of light when tetrachlorobenzylidene chloride $\text{C}_6\text{HCl}_4\cdot\text{CHCl}_2$ is formed. This when dissolved in strong sulphuric acid and the solution poured into ice-cold water

yields tetrachlorobenzaldehyde, which may be purified by means of its bisulphite compound. Forms colourless needles; m.p. 97°–98° (Cassella, Eng. Pat. 16317, 1914).

TETRACHLOROPHTHALIC ACID



Best formed by acting on a mixture of phthalic anhydride, fuming sulphuric acid, and a little iodine with chlorine, and gradually raising the temperature to 200°



The chlorosulphonic acid is removed by distillation and the tetrachlorophthalic anhydride is washed and boiled with sodium carbonate solution. On adding hydrochloric acid tetrachlorophthalic acid is precipitated.

TETRADECYLMALONIC ACID $\text{C}_{17}\text{H}_{32}\text{O}_4$

Prepared by heating α -cyanopalmitic acid with alcoholic potash (Hell and Jordanoff, Ber. 1891, 991), m.p. 117°–118°.

TETRADYMITE or TELLURIC-BISMUTH.

A bismuth telluride often containing some sulphur, the formula usually being $\text{Bi}_2\text{Te}_2\text{S}$ or $2\text{Bi}_2\text{Te}_3 \cdot \text{Bi}_2\text{S}_3$. Traces of selenium and gold are also often present. Crystals are rhombohedral, but small and indistinct and of rare occurrence; they are sometimes twinned in groups of four, hence the name, from $\tau\epsilon\tau\rho\alpha\delta\upsilon\mu\omicron\varsigma$, fourfold. A characteristic feature of the mineral is the highly perfect cleavage parallel to the basal plane. The laminae are flexible, not very sectile, and soft enough ($\text{H.} = 1\frac{1}{2}$ –2) to be scratched by the finger-nail and to mark paper. The colour is light steel-grey with a brilliant metallic lustre. Usually the mineral occurs as foliated masses of irregular outline embedded in massive quartz, more especially in veins of gold-quartz. Before the blowpipe, the mineral fuses readily and is entirely volatilised; it is readily soluble in nitric acid with separation of sulphur. The following table gives the composition of typical tetradymite (anal. II) and of some other closely related minerals of identical appearance. I, sulphur-free tetradymite from Dahlonga, Georgia, Bi_2Te_3 (Balch, 1863); II, crystals of tetradymite from Schubkau, near Schemnitz in Hungary, $\text{Bi}_2\text{Te}_2\text{S}$ (W. Muthmann and R. Schröder, 1897); III, *wehrlite* from Deutsch-Pilsen, Hungary, also Ag 0.48, $\text{Bi}_8\text{Te}_5\text{S}$ or Bi_3Te_2 (Sipöcz, 1885); IV, *joséite* from San José, Minas Geraes, Brazil, $\text{Bi}_8\text{Te}_3\text{S}_2$ (A. Damour, 1845); V, *grünlingite* from Brandy Gill, Carrock Fell, Cumberland, $\text{Bi}_4\text{S}_3\text{Te}$ or $\text{Bi}(\text{S},\text{Te})$ (W. Muthmann and R. Schröder, 1897).

	I.	II.	III.	IV.	V.
Bi .	51.51	59.98	70.02	79.15	78.82
Te .	48.50	35.35	28.52	15.93	12.66
Se .	—	trace	—	1.48	—
S .	—	4.35	1.33	3.15	9.40
	100.01	99.68	100.35	99.71	100.88
Sp. gr.	7.64	7.09	8.4	7.93	7.32

In addition to the localities given above, mention may be made of Mount Shamrock in

Queensland, and Sorata in Bolivia, where larger masses, associated with native bismuth and bismuth-glance, are found. Another British locality is the Glogau gold mine near Dolgelly.

L. J. S.

TETRAETHYLDIAMINO BENZOPHENONE v. KETONES.

TETRAHEDRITE v. FAHL-ORE.

TETRAHYDROCOLCHICIN. Catalytic reduction product of colchicin.

TETRAHYDRONAPHTHALENE (TETRALIN) AND ITS DERIVATIVES. The existence of hydrogenated naphthalene derivatives in coal tar has been demonstrated by the isolation of tetrahydronaphthalene from the hydrocarbon fraction containing indene and coumarone by sulphonation, followed by the hydrolysis of the sulphonic acid with steam (Berthelot, Ann. Chim. 1867, (4) 12, 193; Bull. Soc. chim. 1868, (2) 9, 228; Kramer and Spilker, Ber. 1896, 29, 561; Boes, Ber. Deut. pharm. Ges. 1902, 12, 222; Stoermer and Kahlert, Ber. 1902, 35, 1632).

The methods which are available for the preparation of hydrogenated derivatives of naphthalene fall into the following three classes:

(1) *Reduction with hydriodic acid.*—The products, $\text{C}_{10}\text{H}_{10}$ and $\text{C}_{10}\text{H}_{12}$, were isolated by Berthelot (Bull. Soc. chim. *l.c.*) by heating naphthalene with hydriodic acid at 280°, whilst a product of the latter formula, b.p. 201°, was obtained by Baeyer (Annalen, 1870, 155, 276) by heating naphthalene and phosphonium iodide at 170°–190°. Graebe (Ber. 1872, 5, 678) obtained tetrahydronaphthalene, b.p. 205°, by heating naphthalene with hydriodic acid and phosphorus at 220°–250°, but Agrestini (Gazz. chim. ital. 1883, 12, 495), who repeated this experiment at 235°, obtained hexahydronaphthalene, and it was shown subsequently by Graebe and Guye (Ber. 1883, 16, 3028) that the reaction product was dependent on the temperature, tetrahydronaphthalene being formed at 210°–225°, and hexahydronaphthalene at 240°–250°. The latter authors were, moreover, unable to isolate any dihydronaphthalene when phosphorus was used. Wreden (Annalen, 1887, 187, 164) repeated Berthelot's experiments and obtained a mixture of hydrocarbons, b.p. 55°–300°, from which he isolated a hydrocarbon, $\text{C}_{10}\text{H}_{20}$, which he called hexahydrocymene, whilst by heating naphthalene with hydriodic acid and phosphorus at 260° for 36 hours he obtained a hydrocarbon, $\text{C}_{10}\text{H}_{18}$, b.p. 173°–180°, which he named dcahydronaphthalene (J. Russ. Phys. Chem. Soc. 1876, 8, 149). Ross and Leather (Analyst, 1912, 31, 248) obtained a similar compound, b.p. 170°–173°, by heating the mixture at 210° for 4 days. These methods, however, possess numerous disadvantages, and it is doubtful whether any of these products were pure (Schroeter, Annalen, 1922, 428, 5).

Moreover, it would appear that the tetrahydro-derivative of naphthalene obtained by the action of phosphorus and hydriodic acid on naphthalene is 1:4:5:8-tetrahydronaphthalene (α -tetrahydronaphthalene), whereas other methods of preparation give rise to 1:2:3:4-tetrahydronaphthalene (β -tetrahydronaphthalene) (Baly and Tuck, Chem. Soc. Trans. 1908, 93, 1902).

(2) *Reduction with sodium.*—Bamberger and Lodter (Ber. 1887, 20, 3075) obtained the hydro-

carbon, $C_{10}H_{10}$, Δ^2 -dihydronaphthalene, or 1:4-dihydronaphthalene by the action of sodium and ethyl alcohol on naphthalene, whilst Bamberger and Kitchelt (Ber. 1890, 23, 1561) found that tetrahydronaphthalene was formed when amyl alcohol was used in place of ethyl alcohol. Straus and Lemmel (Ber. 1913, 46, 232; Straus, *ibid.* 1051) showed that Δ^2 -dihydronaphthalene is converted into Δ^1 -dihydronaphthalene, or 1:2-dihydronaphthalene, by heating with sodium ethylate, and that this isomeride can be further reduced to tetrahydronaphthalene by the action of sodium and ethyl alcohol, results which were confirmed and extended by Rowe (J. Soc. Chem. Ind. 1920, 39, 241 T).

F. Bayer & Co. (D. R. PP. 305347, 306724, 1916) prepared tetrahydronaphthalene by heating a solution of naphthalene in solvent naphtha with sodium and ethyl alcohol at a high temperature. Tetrahydronaphthalene is obtained also by the use of water in place of ethyl alcohol, but the replacement of solvent naphtha by a mixture of aliphatic hydrocarbons, b.p. 115° – 120° , results in the formation of dihydronaphthalene (Chem. Fabr. Griesheim-Elektron, D. R. P. 370974). Sachs (Ber. 1906, 39, 3013) prepared tetrahydronaphthalene by the action of sodamide on naphthalene, whilst Lebeau and Pichon (Compt. rend. 1914, 158, 1514) obtained tetrahydronaphthalene in 90 p.c. yield by enclosing a mixture of liquefied ammonia, sodium, and naphthalene in an autoclave and allowing it slowly to attain the air temperature. The sodamide formed in this reaction must influence the course of the hydrogenation, for nascent hydrogen alone does not convert naphthalene into tetrahydronaphthalene (Schlubach, Ber. 1915, 48, 12). Methods in which sodium is used require a large excess of sodium for complete hydrogenation to the tetrahydro-stage.

The tetrahydronaphthalene obtained by Graebe and by Baeyer using hydriodic acid, and the tetrahydronaphthalene obtained by Bamberger using sodium, have been regarded as different products, viz. 1:4:5:8- and 1:2:3:4-tetrahydronaphthalene respectively; the view that these compounds were not identical was based upon the difference in the crystalline form and content of water of crystallisation of the barium sulphonate, and the odour of the hydrocarbon (*cf.* Leroux, Ann. Chim. 1910, (8) 21, 458).

(3) *Reduction with hydrogen in the presence of a catalyst.*—The hydrogenation of naphthalene and its derivatives by means of hydrogen in the presence of a catalyst may be classified in three main divisions, viz. (a) *Reduction in the vapour phase.* Sabatier and Senderens (Compt. rend. 1901, 132, 1254) found that tetrahydronaphthalene was formed when a mixture of naphthalene vapour and hydrogen was passed over reduced nickel at 200° , whilst Leroux (Compt. rend. 1904, 139, 672; Ann. Chim. *l.c.*) also obtained tetrahydronaphthalene at 200° , and by using nickel, reduced at 250° , obtained decahydronaphthalene at 160° in a similar manner. The latter compound, however, differed in its physical properties from the compound described by Wreden (*l.c.*). Zelinski (Ber. 1923, 56, 1723) has prepared decahydronaphthalene smoothly by passing tetrahydronaphthalene and hydrogen

over platinised asbestos at 150° – 160° , or over palladium black at 120° . Decahydronaphthalene, however, is dehydrogenated very readily by palladium black at 300° under atmospheric pressure with formation of naphthalene, but no formation of intermediate products of an unsaturated character was observed. Leroux also applied the method of Sabatier and Senderens to α - and β -naphthol at temperatures below 200° when the corresponding decahydro-derivatives were obtained (Compt. rend. 1905, 140, 590; *ibid.* 141, 953). Padoa and Fabris (Atti R. Acead. Lincei, 1908, (5) 17, i. 111; *ibid.* ii. 125) obtained tetrahydronaphthalene in a similar manner at 200° , and they showed that at 300° naphthalene undergoes no hydrogenation. Sabatier and Mailhe (Fr. Pat. 477212, 1914) found that naphthalene vapour is partially decomposed into carbon and hydrogen by passing over catalysts, such as metallic powders deposited on an inert substratum not containing silica, at 500° – 1000° , and that the mixture of hydrogen and naphthalene vapour formed, when passed over a second catalyst, such as a metallic powder or alloy on a suitable substratum, yields a mixture of tetra- to decahydronaphthalenes, together with naphthalene. (b) *Reduction in the liquid phase.* Ipatiew (Ber. 1907, 40, 1287) obtained tetrahydronaphthalene by heating naphthalene with hydrogen under 181 atmospheres pressure in the presence of nickel oxide, Ni_2O_3 , at 260° for 24 hours, whilst by heating naphthalene under a hydrogen pressure of 178 atmospheres for 12 hours at 230° decahydronaphthalene was obtained. In a similar manner the same author obtained decahydro- α -naphthol and decahydro- β -naphthol, nickelic oxide proving a better catalyst than nickelous oxide, both of which catalysts, however, bring about the catalytic hydrogenation of naphthalene, α - and β -naphthol, more quickly than reduced nickel (J. Russ. Phys. Chem. Soc. 1907, 39, 693). Wimmer (D. R. PP. 300052, 302488, 1915) obtained decahydronaphthalene at 180° – 200° under a hydrogen pressure of 15–30 atmospheres by using a catalyst obtained by heating nickel formate, either dry or in a saturated glyceride with hydrogen. (c) *Reduction in a suitable organic solvent.* Decahydronaphthalene was obtained by Willstätter and Hatt (Ber. 1912, 45, 1474) by shaking an ethereal or glacial acetic acid solution of naphthalene with platinum black, but the purest commercial naphthalene, which contained 0.25 p.c. of sulphur, was unaffected under these conditions. Moreover, Willstätter and King (Ber. 1913, 46, 527) found that tetrahydronaphthalene was not formed at any stage of the process, but that a mixture of naphthalene and decahydronaphthalene was always obtained until all the naphthalene was converted into decahydronaphthalene. The same authors, however, obtained tetrahydronaphthalene by the same method from pure dihydronaphthalene, which they believed to be 1:4-dihydronaphthalene but which was actually the 1:2-isomeride (Straus, *l.c.*). Straus and Lemmel (Ber. 1921, 54, 25), on the other hand, found that tetrahydronaphthalene was formed from 1:2-dihydronaphthalene by the action of hydrogen in presence of palladium and ethyl alcohol, whereas the use of platinum and glacial acetic acid leads to the formation of higher

hydro-compounds. Skita and Meyer (Ber. 1912, 45, 3592) obtained decahydronaphthalene by the action of hydrogen on a glacial acetic acid-etheral solution of naphthalene in the presence of colloidal platinum using gum arabic as stabilising colloid. Rowe (*l.c.*) has obtained 1:4-dihydronaphthalene by the action of hydrogen on an ethyl alcoholic solution of naphthalene in the presence of nickel deposited on kieselguhr.

As the preparation of decahydronaphthalene by Willstätter and Hatt, and Willstätter and King appeared at variance with the technical method adopted subsequently for the manufacture of tetrahydronaphthalene, Willstätter and Seitz (Ber. 1923, 56, 1388) repeated the earlier experiments. It was found that the hydrogenation of naphthalene with hydrogen in presence of spongy platinum is affected greatly by the proportion of oxygen present in the catalyst or in the hydrogen used. No hydrogenation occurs in the absence of oxygen, whereas tetrahydronaphthalene is the main product in presence of a minimum quantity, or of a considerable quantity, of oxygen, whilst decahydronaphthalene is the main product, without the formation of any detectable intermediate product, when oxygen is present in relatively small quantity. This result is explained by the assumption that in presence of spongy platinum intermediate dihydro-derivatives, such as 1:2-, 1:4-, or 1:5-dihydronaphthalenes, are formed. Of these, 1:2-dihydronaphthalene is the most stable, and is the probable intermediate product in the formation of tetrahydronaphthalene in presence of platinum rich in oxygen. A dihydro-derivative containing the hydrogen atoms attached to both nuclei, such as 1:5-dihydronaphthalene, may be formed momentarily in presence of spongy platinum poor in oxygen, and then perhydrogenated immediately, whereas a dihydro-derivative of this type is dehydrogenated readily in presence of spongy platinum rich in oxygen.

This series of investigations laid a sure foundation for the development of a technical method for the hydrogenation of naphthalene which, as a result of the work of Schroeter, von Gwinner and Schrauth, and other collaborators, culminated in the process adopted by Tetralin, G.m.b.H., at the works in Rodleben, near Rossau, Germany, where plant has been installed with a daily capacity of 120 tons of tetralin (tetrahydronaphthalene). The great obstacle to the technical hydrogenation of naphthalene was the difficulty of purification, and Fischer, Schneider and Hilpert (Ber. 1916, 49, 252) considered that the catalytic hydrogenation of naphthalene was practically out of the question on account of the sulphur content, even in the case of technically pure naphthalene. This difficulty has been overcome, however, by the removal of the thionaphthenes and similar sulphur-containing substances by heating with absorbent materials, such as fuller's earth, kieselguhr, &c., together with a readily fusible metal, such as sodium, or with finely divided nickel, carbides, or amides. Naphthalene, purified in this manner, is distilled into the hydrogenating autoclaves, and treated with hydrogen at 180°–200° under a pressure of 225 lbs., in the presence of nickel deposited on an inert medium.

The reaction may be stopped at the tetrahydro-stage or may be continued to produce decahydronaphthalene (decalin). A mixture of tetrahydro- and decahydronaphthalenes is placed on the market under the name of Tetralin Extra or Tetralin Essence, and, if necessary, the tetrahydro-derivative can be separated from the more highly hydrogenated derivatives by solution in liquid sulphur dioxide.

Applications of hydronaphthalenes.—The cost of naphthalene is so low that its conversion into liquid hydrogenated hydrocarbons is undoubtedly economically practicable. Tetralin or tetralin extra have been proposed as substitutes for turpentine (Vollmann, *Färber-Zeit.* 1919, 24, 1689), as the high boiling-point and low volatility simplify the manufacture of lacquers and varnishes of good covering power, whilst tetralin extra serves as an oxygen-carrier. There has, however, been so much controversy on this question that the practical utility as a turpentine substitute is open to doubt. Tetralin and decalin may be used alone as a lubricant or in conjunction with other lubricants (D. R. P. 306836, 1916), whilst viscous lubricating oils may be manufactured by the condensation of an alkyl or acid chloride with tetrahydronaphthalene (D. R. P. 319799, 1917), and an even better product is that obtained by the interaction of a chloro-derivative of tetrahydronaphthalene with tetrahydronaphthalene in the presence of phosphorus pentoxide at 180°. The latter product is a viscous oil, b.p. 240°–243°/15 mm., sp.gr. 1.104/15°, viscosity 35.5° (Engler) at 50°. When sulphonated it yields a good soluble oil. Tetralin and decalin have been used to some extent as fuel for internal combustion engines, and as oils for burning. Although the calorific value of the latter product is 10,800 as compared with 10,000 for benzene, the high flash point is a serious objection, whilst it is unlikely to be able to compete as a motor fuel under normal conditions. Tetralin alone or mixed with other burning oils can be burnt in an ordinary paraffin lamp, giving a highly luminous flame with no burner troubles (Wimmer, D. R. P. 302488, 1915), but it could scarcely compete normally with kerosene. In this connection, see Fischer, Schneider and Hilpert (*l.c.*), who showed that hydronaphthalene derivatives are also formed by heating naphthalene with 4 p.c. of its weight of aluminium chloride in an autoclave for a short time at about 330°, and found that the fraction, b.p. 150°–300°, had a calorific value of 9932, viscosity of 1.16/20°, flash point 70°–75°, and would serve as an illuminant in a burner with a powerful draught, such as is designed for Russian oil.

The use of tetralin as a solvent for resins, fats, essential oils, liquid and solid hydrocarbons, rubber, sulphur, dyes, &c., has been proposed (Tetralin, G.m.b.H., D. R. P. 320807, 1916), and it is used to some extent as a solvent or diluent in the preparation of boot polishes and waxes. Tetralin mixed with amyl alcohol and other solvents is useful for the removal of dried paint films, varnishes, &c. (Tetralin, G.m.b.H., D. R. P. 320152, 1918).

Comparative experiments with turpentine, tetralin (tetrahydronaphthalene), and a tetralin-benzene (3:1) mixture in white lead, lithopone and metallic ochre paints showed that they

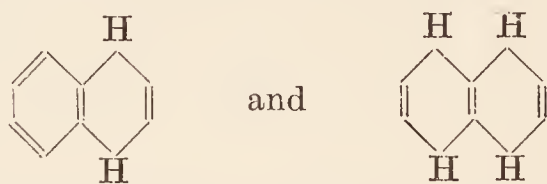
had equal drying properties, drying to hard films on both glass and oiled wood in 20 hours. Tetralin was also tested with great success in a number of oil-varnishes for both interior and exterior work. The red-tinting complained of in certain white varnishes in which tetralin was used is not in any way due to the tetralin, but probably due to some adulterant of one of the resins employed, to a resin actually present in the wood painted, or to the presence of traces of sesamé oil (Rasser, Chem. Zeit. 1923, 47, 660).

Tetralin is a valuable crystallising medium, particularly for substances which dissolve with difficulty in other solvents. Tetrahydronaphthalene and its derivatives may well prove of importance in the future for the production of dyes.

THE COURSE OF THE REACTION IN THE HYDROGENATION OF NAPHTHALENE AND ITS DERIVATIVES.

(1) *Reduction with hydriodic acid.*—The reduction of naphthalene with hydriodic acid appears to proceed in stages, by each of which two atoms of hydrogen are added to the molecule, and the particular main product obtained in passing from naphthalene to decahydronaphthalene appears to be dependent on the conditions which are employed, such as the temperature and the duration of the experiment. If the reaction is carried out in the presence of phosphorus, on the other hand, it does not appear possible to limit it to the formation of dihydronaphthalene, and although Berthelot obtained dihydronaphthalene by heating naphthalene with hydriodic acid, it is possible that this is formed by the action of free iodine on higher hydro-derivatives. There is no doubt that, during the prolonged heating of naphthalene with hydriodic acid at high temperatures, the reaction is not limited to the simple addition of hydrogen to the naphthalene nucleus, but that it is complicated by other changes occurring after the various hydro-derivatives have been formed.

Baly and Tuck (Chem. Soc. Trans. 1908, 93, 1905) consider that the first stages of the hydrogenation when hydriodic acid is used are :

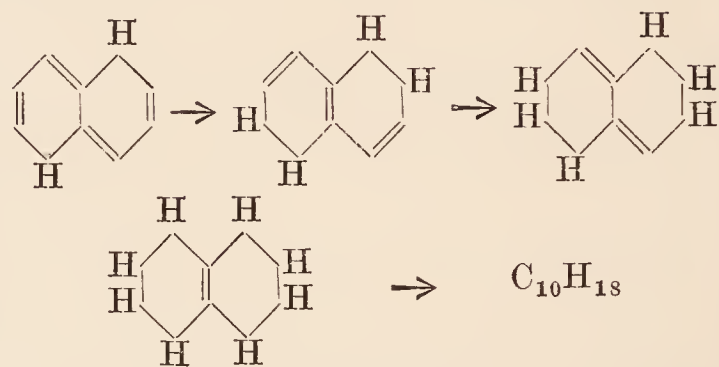


(2) *Reduction with hydrogen in presence of a catalyst.*—The particular hydro-derivative of naphthalene which is obtained by this method of hydrogenation appears to be entirely dependent upon the conditions under which the reaction is carried out. The product obtained varies according to whether the naphthalene is used in the vapour or liquid phase, or in solution, or whether normal or increased pressure is employed; the product varies with the temperature which is employed and the duration of the reaction; but the nature and oxygen content of the particular catalyst used appear to exert the greatest effect in determining the degree of hydrogenation of the product. Moreover, the question of the product which is obtained by these catalytic processes of hydrogenation is complicated by the fact that when the conditions

of temperature and pressure are varied, dehydrogenation may occur (Padoa and Fabris, Atti R. Accad. Lincei, 1908, (5) 17, i. 111; *ibid.* ii. 125; Wieland, Ber. 1912, 45, 486). The latter author considers that the activation of hydrogen in the presence of a finely divided metal is not due to the production of nascent (atomic) hydrogen, but more probably to the formation of a metallic hydride which reacts additively with the unsaturated substance, thus :

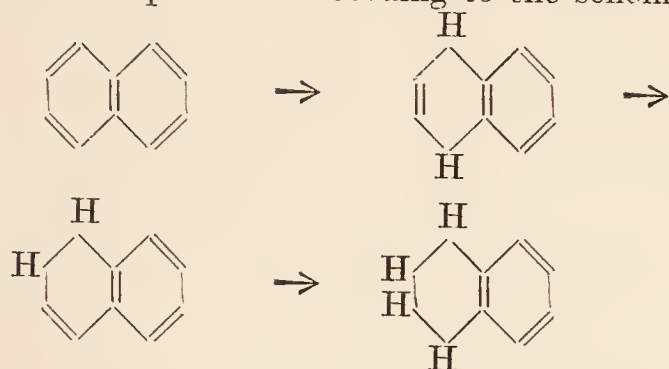


Willstätter and Seitz (Ber. 1923, 56, 1388) consider that when dihydrogenation occurs in one nucleus only, a distinct break occurs at the tetrahydro stage, after which further additions of hydrogen take place more slowly than with naphthalene itself. On the other hand, if it is assumed that a dihydro-derivative is formed in which a hydrogen atom is attached to each nucleus, a series of intermediate products is formed, each of which is less saturated than naphthalene, and hydrogenation continues at a much greater rate than with naphthalene, thus :

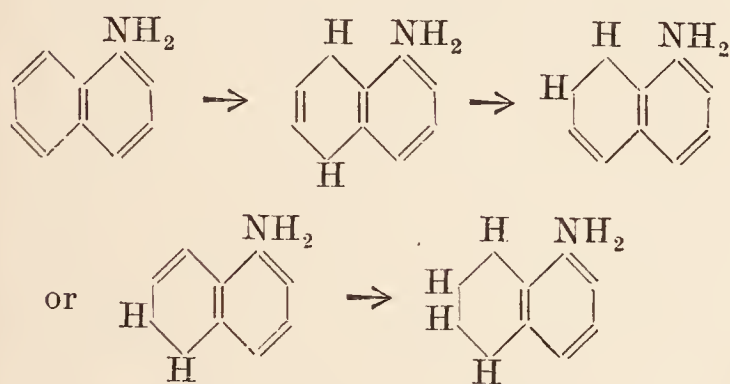


(3) *Reduction with sodium and an alcohol.*—It is quite clear that the hydrogenation of naphthalene and its substituted derivatives with sodium and an alcohol is limited to the production of tetrahydro-compounds as no case has been recorded of the production of a more highly hydrogenated naphthalene derivative by this method, although in the case of a certain hydro-derivative of naphthalene, which has been prepared by a method other than that involving the use of sodium and an alcohol, a further introduction of six atoms of hydrogen may be effected by this method. Thus, *ar*-tetrahydro- β -naphthoic acid, which is not obtained from β -naphthoic acid by the use of sodium and an alcohol, can be reduced further to decahydro- β -naphthoic acid with sodium and amyl alcohol, whereas β -naphthoic acid itself, when hydrogenated by the latter method, gives rise to the alicyclic tetrahydro-derivative. In general, the particular product which is obtained is dependent upon the nature of the alcohol or upon the concentration of the sodium alkoxide employed. When amyl alcohol is used the product is usually a tetrahydronaphthalene derivative, but when any other alcohol is used, either alone or in conjunction with an inert solvent of high boiling-point, the question whether a dihydro- or a tetrahydronaphthalene derivative will be formed is dependent on the concentration of the sodium alkoxide used, and the boiling-point of the mixture. This is due to the fact that the hydrogenation by this method undoubtedly proceeds in stages, as has been proved to be the case for naphthalene, α -naphthylamine, and

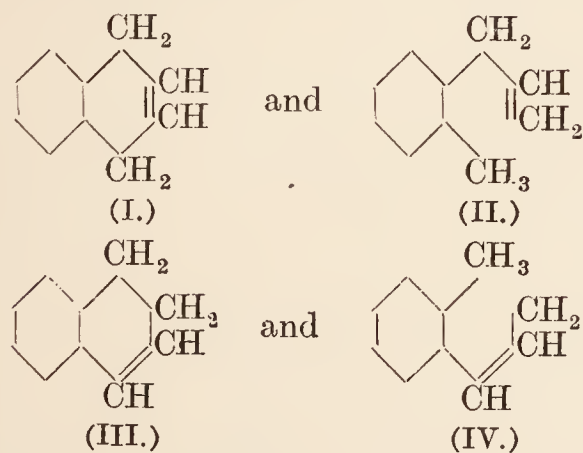
α -naphthol. A dihydro-derivative is formed first in which the two hydrogen atoms occupy the *p*-position with respect to one another, and further hydrogenation does not take place unless the conditions of the reaction are suitable for the preliminary isomerisation of this compound to the dihydro-derivative in which the two hydrogen atoms occupy the *o*-position with respect to one another. In order that this isomerisation may take place, suitable conditions of temperature and concentration of the sodium alkyloxide are essential. The temperature necessary is proportional to the concentration of sodium alkyloxide, for the higher the concentration the lower is the temperature required for isomerisation, whilst both the conditions of temperature and concentration of the sodium alkyloxide vary with the particular alcohol used. Thus, the hydrogenation of naphthalene proceeds according to the scheme :



and of α -naphthylamine according to the scheme :



The difference in properties between 1:4-(I.) and 1:2-dihydronaphthalene (III.), in that only the latter is reduced to tetrahydronaphthalene by sodium and ethyl alcohol, is important. This fact disposes of the difficulty of reconciling the reduction of naphthalene through 1:4-dihydronaphthalene to tetrahydronaphthalene with the behaviour of the analogous allyl-benzene (II.) and propenyl-benzene (IV.)



only the latter of which is reduced by sodium and an alcohol to a saturated homologue of benzene, and consequently 1:4-dihydronaphthalene should not be directly reducible.

The classical investigations of Bamberger and his numerous collaborators on the tetra-

hydrogenation of naphthalene, naphthylamines, and naphthols by means of sodium and amyl alcohol have shown that the four atoms of hydrogen are always added asymmetrically, and are never distributed between the two rings of the naphthalene nucleus. When a substituted naphthalene derivative is hydrogenated in this manner, the product obtained is dependent upon the position of the substituent group in the nucleus. Thus, α -derivatives of naphthalene, e.g. α -naphthylamine, give rise mainly to aromatic (ar.) compounds, which contain the substituent group in one ring and the added hydrogen atoms in the other ring of the naphthalene nucleus, whilst β -derivatives of naphthalene, for example, β -naphthylamine, give rise mainly to alicyclic (ac.) compounds, which contain both the substituent group and the added hydrogen atoms in the same ring of the naphthalene nucleus, together with a limited proportion of the aromatic isomeride. In the case of the hydrogenation of diethyl- β -naphthylamine and of 1-methyl- β -naphthylamine, however, the reverse is the case, for the ar-tetra-hydro-derivative is the main product, whilst the yield of the ac-isomeride is extremely low. The alicyclic amino- or hydroxy-derivatives possess the properties of fatty amines or alcohols, whereas the aromatic derivatives retain the aromatic characteristics of the parent substance, although they have lost certain naphthalenoid properties and approximate more nearly to the corresponding xylene, xylenol, or xylidine. For example, ar-tetrahydro-1:4-naphthylenediamine possesses the properties of a *p*-diamine of the benzene series, for when mixed with aniline hydrochloride and oxidised with bichromate, an indamine and a safranine are formed, whereas such is not the case when 1:4-naphthylenediamine is oxidised under similar conditions. Moreover, the naphthols are converted into alkyl-derivatives when heated with an alcohol and hydrochloric acid at 130°, but ar-tetrahydronaphthols resemble phenol and most of its homologues in that they do not react under similar conditions. Further, the naphthaquinones form hydrazones with phenylhydrazine, but ar-tetrahydro- α -naphthaquinone, which resembles benzoquinone in its odour, volatility, colour, and crystalline form, under similar conditions is reduced to ar-tetrahydro- α -naphthahydroquinone. With regard to the resemblance between alicyclic tetrahydro-compounds and fatty amines or alcohols, ac-tetrahydro- α -naphthylamine possesses similar properties to phenylethylamine. This similarity is particularly marked in the case of the nitrites, which can be crystallised from boiling water, and are converted, with elimination of ammonia, into the unsaturated hydrocarbons, Δ^1 -dihydronaphthalene and cinnamene, respectively. On these grounds, Bamberger regarded naphthalene, and those of its derivatives, in which each of the eight carbon atoms is united with a monovalent radicle, as containing two carbon systems, neither of which exists as a benzene ring, but one of which is converted into a benzene ring when four hydrogen atoms are added to the other system. The effect of the addition of four atoms of hydrogen to one of the two carbon systems in naphthalene or its derivatives is to cause that system to exhibit

the character of an open fatty chain. Consequently, tetrahydronaphthalene derivatives possess the characteristics of a benzene derivative with a fatty side chain, the hydrogenated system acquiring fatty functions, and the non-hydrogenated system acquiring benzenoid functions. In Bamberger's view the various formulæ proposed for naphthalene were inadequate, as they failed to explain the conversion by reduction of a ring system similar to benzene into one identical with it, and this led him to propose his centric formula for naphthalene, although his views on this subject were modified somewhat subsequently.

Δ^2 -Dihydronaphthalene or 1:4-dihydronaphthalene occurs in heavy coal-tar oil (Berthelot, l.c.). It is formed by heating naphthalene with 20 parts of concentrated hydriodic acid at 280° for a short time (Berthelot). This compound appeared to be identical with that obtained by Graebe and Guye (Ber. 1872, 5, 678; *ibid.* 1883, 16, 3028) by distilling the oily product obtained by the action of bromine on tetrahydronaphthalene. Von Pechmann (Ber. 1883, 16, 516), by distilling with soda lime the product obtained by the action of sulphuric acid on benzyl-acetate, obtained a compound which he considered also to be identical with the dihydronaphthalene of Berthelot, but Roser (Ber. 1887, 20, 1575) states that the former compound is α (?)-methyl-indonaphthene. The preparation of a dihydronaphthalene by the action of calcium and absolute alcohol on naphthalene has been described by Marschalk and Nicolajewsky (Ber. 1910, 43, 1701).

Δ^2 -Dihydronaphthalene is obtained as a by-product by the action of sodium and ethyl alcohol on α - and β -naphthonitrile (Bamberger and Lodter, Ber. 1887, 20, 1703; Bamberger and Boekmann, *ibid.* 1711); by the action of hydrogen on an ethyl alcoholic solution of naphthalene in the presence of nickel (Rowe, J. Soc. Chem. Ind. 1920, 39, 241 T); from α -5:8-dihydro- α -naphthylamine by the diazo-reaction (Rowe and Levin, Chem. Soc. Trans. 1920, 117, 1577); by the action of zinc on an alcoholic solution of ac-2:3-dibromotetrahydronaphthalene (Straus, Ber. 1913, 46, 1051). Its formation from ac-tetrahydronaphthalene derivatives by the elimination of water, ammonia, hydrogen chloride, &c., has been described on numerous occasions, but there is no doubt that the compound prepared by such methods is actually the isomeride, 1:2-dihydronaphthalene. The preparation of crude 1:4-dihydronaphthalene is best carried out by the method of Bamberger and Lodter (Ber. 1887, 20, 3075; Annalen, 1895, 288, 75) by the action of sodium on an ethyl alcoholic solution of naphthalene. The product, which is a complex mixture of naphthalene, dihydronaphthalenes, and tetrahydronaphthalene, is purified as described by Sand and Gennsler (Ber. 1903, 36, 3706) by shaking an ethereal solution with an aqueous solution of mercuric acetate for 24 hours, when the 1:4-dihydronaphthalene only forms a crystalline mercury compound soluble in benzene. This *mercury compound*, colourless needles, m.p. 122°, yields a *bromide*, glistening needles, m.p. 159°, and an *iodide*, m.p. 156°, all of which when decomposed with hydrochloric acid yield pure 1:4-dihydronaphthalene.

1:4-Dihydronaphthalene, colourless plates volatile with steam, m.p. 24.5°–25°, b.p. 94.5°/17 mm. (Straus and Lemmel, Ber. 1913, 46, 232), m.p. 24.5°–24.8° (Straus), m.p. 25°, b.p. 84°/9.5 mm., d_4^{20} 1.005 (von Auwers, Ber. 1913, 46, 2988), molecular heat of combustion at constant pressure 1299.8/20.7° (Roth and von Auwers, Annalen, 1915, 407, 145; cf. Leroux, Compt. rend. 1910, 151, 384); its constitution was determined by oxidation for, on treatment with potassium permanganate, it yields *o*-phenylene-diacetic acid; 1:4-dihydronaphthalene does not form a picrate. When 1:4-dihydronaphthalene is brominated in cold chloroform solution, ac-2:3-dibromotetrahydronaphthalene (1:4-dihydronaphthalene dibromide) is formed together with a small quantity of an oil. ac-2:3-Dibromotetrahydronaphthalene crystallises in large transparent colourless prisms, m.p. 71.5°–72° (Straus and Lemmel). A considerable amount of confusion has arisen with regard to the two isomeric dihydronaphthalenes on account of the proximity of the melting-points of their dibromides, viz. 71.5°–72° and 70°–71° respectively, which have been used for the identification of the hydrocarbons, although actually when the crystals are compared there is no difficulty in differentiation. A further difference is that ac-2:3-dibromotetrahydronaphthalene when boiled with methyl alcohol yields a neutral solution, whereas the methyl alcoholic solution of the isomeric ac-1:2-dibromotetrahydronaphthalene after similar treatment becomes acidic. ac-2:3-Dibromotetrahydronaphthalene is readily converted by heat, concentrated sulphuric acid, or alcoholic potash into naphthalene, with elimination of hydrogen bromide, and when an alcoholic solution is treated carefully with zinc-dust at 55°–60° pure 1:4-dihydronaphthalene is obtained, whilst decomposition products are formed if the mixture is boiled too vigorously (Straus and Lemmel; Bamberger and Lodter; Willstätter and King, Ber. 1913, 46, 527).

ac-2:3-Dihydroxytetrahydronaphthalene (or tetrahydronaphthalene glycol), which Leroux (Compt. rend. 1909, 148, 931; Ann. Chim. 1910, (8), 21, 458) considers to be the *cis*-glycol, is obtained by the action of potassium carbonate on ac-2:3-dibromotetrahydronaphthalene; by heating a mixture of tetrahydronaphthalene-2:3-oxide and water for 6–8 hours at 120°, followed by distillation with steam to remove any unchanged oxide; by boiling a mixture of the oxide with dilute sulphuric acid for 24 hours; in 95 p.c. yield, by heating a mixture of the oxide and dilute acetic acid (1:16) for about 6 hours on the water-bath; by the action of alkalis on the chlorohydrin, ac-2-chloro-3-hydroxytetrahydronaphthalene, or the corresponding iodohydrin.

ac-2:3-Dihydroxytetrahydronaphthalene crystallises in silvery plates, m.p. 135°, and is not volatile with steam. It resembles naphthalene in appearance, is insoluble in alkalis, and does not condense with diazonium salts; on oxidation it yields *o*-phenylene-diacetic acid, together with smaller amounts of *o*-carboxy-phenyl-acetic acid and other products. ac-2:3-Dihydroxytetrahydronaphthalene forms a *dibenzoate*, large prisms, m.p. 89°–90° (Bamberger and Lodter), or 91° (Leroux); a *diacetate*, transparent monoclinic prisms, m.p. 109.5°–110° (Bamberger and

Lodter), or 111° (Leroux); a *bisphenylurethane*, fine needles, m.p. 148° – 150° (Bamberger and Lodter), or 150° (Leroux) (Bamberger and Lodter, Ber. 1893, 26, 1833; Bamberger and Voss, *ibid.* 1894, 27, 1547; Bamberger, Lodter and Diecke, Annalen, 1895, 288, 74–133). On treating ac-2 : 3-dibromotetrahydronaphthalene in acetic acid solution with silver acetate, an ester is obtained which, on hydrolysis, yields a mixture of glycols isomeric with the product obtained by Bamberger. The product melts at 110° , and by repeated crystallisation from benzene may be separated into *cis-trans-ac-2 : 3-dihydroxytetrahydronaphthalene*, striated tablets, not volatile with steam, m.p. 120° (which forms a *diacetate*, prisms, m.p. 59° , a *dibenzoate*, m.p. 126° , a *bisphenylurethane*, needles, m.p. 175°) and a *substance*, m.p. 140° . The latter compound, which possesses many remarkable properties quite different from those of either of its components, and which Leroux regards as a body of definite composition, is a mixture of the *cis*- and *cis-trans* glycols, and on treatment with acetic anhydride and pyridine yields a mixture of *cis*- and *cis-trans* diacetates. Both the glycols form *o*-phenylene-diacetic acid on oxidation with permanganate (Leroux, *l.c.*).

ac-2-Bromo-3-hydroxytetrahydronaphthalene (or *ac-tetrahydronaphthalene bromohydrin*), snow white needles, m.p. 106° – 106.5° , is obtained by mixing a solution of *ac-tetrahydronaphthylene-2 : 3-oxide* in light petroleum with concentrated hydrobromic acid (Bamberger and Lodter, *l.c.*). Leroux (Compt. rend. 1904, 139, 672; Ann. Chim. 1910 (8), 21, 458) obtained *ac-tetrahydronaphthalene bromohydrin*, prisms, m.p. 112° , by the action of bromine on *tetrahydronaphthalene*, and he considers it to be identical with that of Bamberger and Lodter. The corresponding *iodohydrin*, colourless prisms, m.p. 120° , is obtained by the action of nascent hypoiodous acid on 1 : 4-dihydronaphthalene. Δ^2 -Dihydronaphthalene, when treated with bromotrinitromethane in methyl alcoholic solution, yields a *bromomethoxytetrahydronaphthalene*, colourless liquid, b.p. 115° /0.8 mm. (Schmidt, Bartholomé and Lübke, Ber. 1922, 55, 2099). *ac-2-Chloro-3-hydroxytetrahydronaphthalene* (or *ac-tetrahydronaphthalene chlorohydrin*), long silky needles, which sublime readily at 100° and melt at 117.5° , is obtained by passing dry hydrogen chloride through the fused glycol for about 6 hours at 150° – 160° ; or, better, by the action of hypochlorous acid on 1 : 4-dihydronaphthalene. It is very volatile with steam, and yields an *acetate*, radiating groups of prisms, m.p. 47° , which is converted into the corresponding *oxide* on treatment in the cold with hydrochloric acid; and a *benzoate*, rosettes of needles, m.p. 64° – 65° , which is converted similarly into the *oxide* on treatment with hydrochloric acid. The action of alkalis on the *chlorohydrin* is of a complicated nature, and the products, which vary with the conditions, include *ac-tetrahydronaphthalene-2 : 3-oxide*, *ac-dihydro- β -naphthol*, *ac-tetrahydronaphthylene-2 : 3-glycol*, *ac-tetrahydronaphthylene- m -glycol*, *ac- β -keto-tetrahydronaphthalene*, *naphthalene* and *β -naphthol*. The product most readily formed is *ac-tetrahydronaphthylene-2 : 3-oxide*, which is dimorphous, crystallising in thick plates, which belong either to the monosymmetric

or asymmetric system according to the conditions of crystallisation. It melts at 43.5° , and boils at 257° – 259° /715 mm., and is readily volatile with steam. When heated with hydriodic acid (b.p. 127°) and red phosphorus at 180° for 8 hours it is converted into *tetrahydronaphthalene*, b.p. 204° – 205° /722 mm. Like ethylene oxide, it does not react with hydroxylamine or phenylhydrazine, but combines readily with hydrogen chloride or hydrogen cyanide, and also very readily with organic bases, to form alkynes or alkamines, and less readily with water to form the glycol.

ac-2-Dimethylamino-3-hydroxytetrahydronaphthalene (or *dimethyl-tetrahydronaphthylalkamine*), is an alkaline oil, b.p. 183° /27 mm.; *hydrochloride*, glistening needles, m.p. 180° – 181° ; *aurochloride*, yellow glistening needles; *platinochloride*, orange-yellow leaflets; *picrate*, satiny flat needles, m.p. 182° ; *methiodide*, long lustrous needles, m.p. 201° ; *benzoate* has powerful toxic properties. *ac-2-Diethylamino-3-hydroxy-tetrahydronaphthalene* is a colourless alkaline oil, which develops a fish-like odour on keeping, volatile with steam, b.p. 202° /38 mm.; *hydrochloride*, glistening prisms, m.p. 167° – 170° ; *picrate*, brittle glistening needles, m.p. 170.5° – 171° ; *aurochloride*, yellow leaflets or needles; *platinochloride* is orange-red in colour; *methiodide*, glistening plates, m.p. 151.5° ; *benzoyl derivative*, which forms a *picrate*, yellow needles. *ac-2-Piperidyl-3-hydroxy-tetrahydronaphthalene* forms colourless flaky needles, m.p. 46° – 48° ; *aurochloride*, yellow glistening plates; *platinochloride*, orange-red crystals. *ac-Trimethyl-3-hydroxy-tetrahydronaphthalene hydroxide* forms an alkaline syrup, which crystallises with difficulty in needles; *chloride*, lustrous monosymmetric prisms, m.p. 243° (decomp.), resembles choline in its properties and forms precipitates similar to those obtained with choline when the chloride is treated with the common reagents used for the detection of alkaloids; *platinochloride*, long orange-red needles, m.p. 222° – 223.5° ; *aurochloride*, lustrous golden-yellow leaflets, m.p. 152° – 154° ; *picrate*, flat yellow needles, m.p. 161° – 162° . *ac-bis- β -Hydroxy-tetrahydronaphthylethylenediamine* forms clusters of white needles, m.p. 201° ; *picrate*, yellow crystalline powder. *ac-bis- β -Hydroxy-tetrahydronaphthylamine*, forms long refractive prisms, m.p. 165° – 166° , volatile with steam; *hydrochloride*, white lustrous needles; *platinochloride*, light orange-yellow needles, m.p. 235° (decomp.); *aurichloride*, lustrous yellow leaflets. *ac-2 : 3-Hydroxy-tetrahydronaphthylamine* is an alkaline oil; *hydrochloride*, groups of colourless needles, m.p. 265° ; *phthalimide* compound is a colourless crystalline powder, m.p. 217° – 218.5° ; *platinochloride*, strongly refracting thick yellowish-red prisms; *aurochloride*, groups of small needles; *picrate*, glistening needles (Bamberger and Lodter, Ber. 1893, 26, 1833; Bamberger, Lodter and Diecke, Annalen, 1895, 288, 74).

The compounds described below are not identical with those prepared by Bamberger, Lodter and Diecke, but are stereoisomerides of these alkamines. Dihydronaphthalene dibromide and carbamide react at 140° to form *dihydronaphthalene-2-imino-oxazolidine*, thin plates, m.p. 158° – 159° ; *hydrochloride*, prismatic plates, m.p. 198° ; *platinichloride*, m.p. 224° .

This oxazolidine can be transformed into the *N*-acetylacetate, plates, m.p. 123°–124°, and then into β -hydroxytetrahydro- β -naphthylamine (or dihydronaphthalene alkamine), thin plates, m.p. 107°–108°; *hydrochloride*, m.p. 215°; *platinichloride*, m.p. 230°; *picrate*, yellow needles, m.p. 191°; *copper derivative* (base)₂, CuO + 2H₂O, violet-red needles, m.p. 176°. *Methyl-dihydronaphthalene-2-imino-oxazolidine*, prepared from the above compound and methyl iodide, forms thin plates, m.p. 66°–68°; *hydriodide*, m.p. 203°. As a by-product, an oily *isomeride* is obtained; *hydrochloride*, m.p. 235°. β -Hydroxytetrahydro- β -naphthylmethylamine, needles, m.p. 85°, is prepared from the above imino-oxazolidine derivative by hydrolysis with 20 p.c. sodium hydroxide; *hydrochloride*, m.p. 214°; *copper derivative* (base)₂, CuO, light reddish-brown crystals, m.p. 218°. β -Hydroxy- β -naphthylmethylamine is an oil; *hydrochloride*, m.p. 224°; *picrate*, yellow crystals, m.p. 160° (Takeda and Kuroda, J. Pharm. Soc. Japan, 1921, 1).

When ac-tetrahydronaphthalene-2:3-chlorohydrin is submitted to the continued action of alkalis the ac-tetrahydronaphthylene-2:3-oxide which is formed first is converted into the isomeric *ac-dihydro- β -naphthol*, m.p. about 33°–35°, b.p. 162°–168°/28 mm. (not obtained in a pure state). It is an unsaturated alicyclic alcohol, insoluble in alkalis, volatile with steam, and does not react with diazonium salts, decolorises permanganate and combines readily with bromine. Mineral acids convert it at once into naphthalene. The reaction with bromine is not one of simple addition, the only brominated product isolated had the composition of a *monobromotetrahydronaphthylene glycol*, m.p. 158.5°, naphthalene and a *substance*, m.p. 44°–47°, not identical with ac-tetrahydronaphthylene-2:3-oxide, being formed simultaneously. *ac-Dihydro- β -naphthol*, on oxidation with alkaline permanganate, yields a mixture of dihydroisocoumarin carboxylic acid and *ac-tetrahydronaphthylene-m-glycol*, an oil, b.p. 175°–178°/20 mm., which on keeping forms white needles, m.p. 49°. The latter substance is also obtained by the action of alcohol on *ac-dihydro- β -naphthol*. It is insoluble in alkalis and is not decomposed by mineral acids. *ac-Tetrahydronaphthalene-2:3-chlorohydrin* is converted by the action of dilute alkalis or by distillation with weak bases, *e.g.* quinoline or magnesium carbonate, into *ac- β -ketotetrahydronaphthalene*. An identical product has been obtained by distilling the calcium salt of phenylene-acetic-propionic acid (obtained, *inter alia*, by the reduction of 2-hydroxy- α -naphthoic acid with sodium in the presence of ethyl alcohol, Einhorn and Lumsden, *Annalen*, 1895, 286, 257), and also by the intramolecular transformation of Δ^1 -dihydronaphthylene oxide—a rearrangement which does not take place very smoothly, but is best effected by passing dry hydrogen chloride into a solution of Δ^1 -dihydronaphthylene oxide in light petroleum. The yield of pure ketone, after purification by means of the bisulphite compound, is 50–60 p.c. (Straus and Rohrbacher, *Ber.* 1921, 54, 40). *ac- β -Ketotetrahydronaphthalene* is obtained in 80–85 p.c. yield by heating the methiodide of *ac-2-dimethylamino-1-hydroxytetrahydronaphthalene* to a temperature

very slightly above its melting-point (von Braun, Braunsdorf and Kirschbaum, *Ber.* 1922, 55, 3648). *ac- β -Ketotetrahydronaphthalene* is a colourless, highly refractive oil, m.p. 18°, b.p. 136°/16 mm. (Bamberger and Voss, *Ber.* 1894, 27, 1547), or m.p. 17°–18°, b.p. 136°–137°/22 mm. (Straus and Rohrbacher), b.p. 140°–145°/40 mm. (Einhorn and Lumsden), b.p. 140°/20 mm. or 130°/10 mm., $d_4^{16.9}$ 1.1055 (von Braun, Braunsdorf and Kirschbaum). It is not very stable in air and acquires an orange-yellow colour, though it may be kept unchanged for days in the absence of light. Its autoxidisability in alkaline solution, by which dark indigo-blue solutions are formed, is very characteristic. The *sodium bisulphite* compound crystallises in lustrous colourless plates; the *phenylhydrazone*, colourless lustrous leaflets, m.p. 107.5°–108° (Bamberger and Voss, *l.c.*), or 107° (Straus and Rohrbacher), is rapidly decomposed by light and gives Bülow's reaction; whilst the *oxime* forms silky lustrous stellate needles, m.p. 87.5°–88° (Bamberger, &c.), or 86.5°–87.5° (Straus and Rohrbacher), and the *semicarbazone* melts at 190°–191° (von Braun, Braunsdorf and Kirschbaum).

Finally, hot concentrated alkaline solutions convert *ac-tetrahydronaphthalene-2:3-chlorohydrin* into naphthalene (Bamberger, Lodter and Diecke, *l.c.*; Bamberger and Lodter, *l.c.*; Bamberger and Voss, *l.c.*; *cf.* Bamberger and Lodter, *Ber.* 1891, 24, 1887).

ac-Tetrahydronaphthyl-phenol, needles, m.p. 129°–130° with previous softening, b.p. 320°, readily volatile with steam at 160°, is formed by the action of concentrated sulphuric acid, with or without an equal part of glacial acetic acid, on a mixture of phenol and 1:4-dihydronaphthalene; *sodium salt*, flocculent crystalline precipitate; *benzoyl derivative*, m.p. 107°–108° (Koenigs, *Ber.* 1891, 24, 179). *ac-Tetrahydronaphthyl-anisole*, long silky needles, m.p. 71°, is obtained by boiling *ac-tetrahydronaphthyl-phenol* with methyl iodide and methyl alcohol (Koenigs and Mai, *Ber.* 1892, 25, 2657). When a mixture of 1:4-dihydronaphthalene and thiophenol in acetic-sulphuric acid solution is kept for two months, and the product poured into water a *sulphide* is obtained which is oxidised by permanganate to *ac-tetrahydronaphthyl phenyl sulphone*, white plates, m.p. 139°. When *ac-tetrahydronaphthylene-2:3-oxide* is condensed with amino-ethyl alcohol, *ac-hydroxy-ethylamino-tetrahydro- β -naphthol* is obtained, and yields, on treatment with condensing agents, *naphthalanmorpholine*, prisms, not very volatile with steam, m.p. 62°–63°, b.p. 312°/754 mm.; *hydrochloride*, prisms, m.p. 275°; *platinochloride*, m.p. 225° (decomp.); *aurichloride*, m.p. 225° (decomp.); *picrate*, m.p. 250° (decomp.); *nitrosoamine*, flattened needles, m.p. 161°; *benzoyl derivative*, leaflets, m.p. 194°. *Naphthalanmorpholine* may be converted into the *methiodide* of *methyl-naphthalanmorpholine*, which, on boiling with 10 p.c. soda, yields *ac-dihydro- β -naphthyl dimethylamino-ethyl ether*, a mobile alkaline oil; *methiodide*, rounded crystalline aggregates, which decompose at 140°. *1'-Hydroxyethylnaphthalanmorpholine*, m.p. 105°–108°, b.p. about 300°/160 mm., is prepared by heating *naphthalanmorpholine* with excess of ethylene oxide at 100°. It is

also formed by the action of hot 60 p.c. sulphuric acid on ac-dihydroxyethylaminotetrahydro- β -naphthol. 1''-Methylnaphthalanmorpholine, melts at 57°–53° and boils at 317°/752 mm.; hydrochloride, crystalline nodules; platinochloride, octahedra or cubes, m.p. 250° (decomp.); aurichloride, m.p. 235°; picrate, m.p. 206°–208°; picrolonate, yellow precipitate; methiodide, flattened needles. Methylnaphthalanmorpholine methyl hydroxide is strongly alkaline and yields a precipitate with the usual reagents for alkalis; picrate, m.p. 206°–208°; platinochloride, octahedra; aurichloride, long flattened needles. 1''-Ethylnaphthalanmorpholine boils at 332°/755 mm.; hydrochloride, prisms, m.p. 237°–238°; picrolonate and platinichloride, decompose at 235° and 220° respectively; methiodide dissociates at 205° (Knorr, Ber. 1899, 32, 742; Annalen, 1899, 307, 171).

Δ^1 -Dihydronaphthalene, or 1:2-dihydronaphthalene is formed by the elimination of hydrogen chloride from ac-tetrahydro- β -chloronaphthalene at 190°–200° (Bamberger and Lodter, Ber. 1890, 23, 210); by the elimination of water from ac-tetrahydro- β -naphthol by fusion with potassium hydroxide at 200° (*ibid.*); by heating ac-tetrahydro- β -naphthylamine nitrite (Bamberger and Müller, Ber. 1888, 21, 1116). It is also formed by the exhaustive methylation of ac-tetrahydro- β -naphthylamine and distilling the quaternary hydroxide obtained (Willstätter and King, Ber. 1913, 46, 527), although in all the preceding cases the product was regarded originally as the isomeride, 1:4-dihydronaphthalene (Straus and Lemmel, Ber. 1913, 46, 232; *ibid.* 1921, 54, 25; Straus, *ibid.* 1913, 46, 1051).

It may be prepared by heating 1:4-dihydronaphthalene with 5 times its volume of 5 p.c. sodium ethoxide at 140°–150° for 8 hours, but it was subsequently shown by Straus (*l.c.*) that both the temperature and the concentration of the sodium ethoxide play a part in this reaction. When 1:4-dihydronaphthalene is heated with 5 p.c. sodium ethoxide at its boiling-point (87°) for 1 hour there is no conversion, whilst a two-thirds conversion takes place at 105°, and at 140° heating for half an hour is sufficient for complete conversion. On the other hand, by using 10 p.c. sodium ethoxide the conversion is complete after heating for 1 hour at 100°–105°. Straus and Lemmel also prepared Δ^1 -dihydronaphthalene by the distillation of potassium Δ^1 -dihydronaphthoate with slaked lime, whilst a substance, $C_{10}H_{20}$, large yellow leaflets with a blue fluorescence, m.p. 97.5°–100°, probably a polymeride, was formed simultaneously. The pure product may be obtained from ac-1:2-dibromotetrahydronaphthalene by the action of magnesium in presence of ether, free from alcohol, or by tin in the presence of alcohol (von Braun, D. R. P. 316218, 1918; von Braun and Kirschbaum, Ber. 1921, 54, 597), or by zinc in the presence of alcohol (Bamberger and Lodter; Straus and Lemmel; Willstätter and King, *l.c.*); and from ar-7:8- or 5:6-dihydro- α -naphthylamine by means of the diazo-reaction (Rowe and Levin, Chem. Soc. Trans. 1920, 117, 1578). von Braun and Kirschbaum also showed that 1:2-dihydronaphthalene could be obtained from ac-1:2-dichlorotetrahydronaphthalene by treatment with zinc and alcohol, but that the con-

version is not so complete as in the case of the corresponding dibromo-compound.

1:2-Dihydronaphthalene crystallises in plates, volatile with steam, m.p. –8° to –7°, b.p. 84°–85°/12 mm. (Straus and Lemmel), m.p. –9°, b.p. 84.5°/16 mm. (Willstätter and King), b.p. 78°/9 mm. (von Auwers, Ber. 1913, 46, 2988), m.p. –8°, b.p. 91°/15 mm. (von Braun and Kirschbaum); d_4^{20} 0.997 (von Auwers, *l.c.*), molecular heat of combustion at constant pressure 1297.8/20.5° (Roth and von Auwers, Annalen, 1915, 407, 145; cf. Leroux, Compt. rend. 1910, 151, 384). 1:2-Dihydronaphthalene possesses the characteristic property of forming an isomorphous mixture with naphthalene, which cannot be separated completely by physical means. As an example, a mixture containing 1.7 p.c. of naphthalene melts at –4.5°, whilst a mixture containing 20 p.c. of naphthalene melts at 20°. 1:2-Dihydronaphthalene differs from the 1:4-isomeride in that, on treatment with mercuric acetate, it is oxidised to a mixture of stereoisomeric glycols with the formation of mercurous acetate, and, moreover, it is readily converted into tetrahydronaphthalene on reduction with sodium and ethyl alcohol. It does not form a picrate, and on oxidation with potassium permanganate yields *o*-carboxyphenyl-propionic acid, whilst on oxidation with potassium permanganate containing magnesium sulphate it yields a mixture of the above acid and ac-cis-cis-1:2-dihydroxy-tetrahydronaphthalene (Straus and Rohrbacher, Ber. 1921, 54, 40). When 1:2-dihydronaphthalene in glacial acetic acid solution is treated with ozone and the di-ozonide formed is decomposed with zinc-dust, the product on distillation yields β -*o*-aldehydophenylpropaldehyde, which is oxidised by alkaline permanganate to *o*-carboxyphenyl-propionic acid, or on treatment with warm dilute sulphuric acid yields indene-2-aldehyde (von Braun and Zobel, Ber. 1923, 56, 2139).

Δ^1 -Dihydronaphthalene dibromide, or ac-1:2-dibromotetrahydronaphthalene, is prepared by the bromination of 1:2-dihydronaphthalene in cold chloroform solution (Straus and Lemmel, Ber. 1913, 46, 232; Straus, *ibid.* 1051), and appears to be the only product isolated when tetrahydronaphthalene is brominated at 100°–140°. In the latter case its formation appears to be independent of the relative proportions of the reagents used (von Braun and Kirschbaum, Ber. 1921, 54, 597; D. R. P. 316218, 1918). Willstätter and King (Ber. 1913, 46, 527), by the action of bromine on 1:2-dihydronaphthalene, obtained as a by-product a small quantity of an oil which crystallised but slowly and which they considered might have the constitution of a cis-trans dibromide. ac-1:2-Dibromotetrahydronaphthalene crystallises in stout colourless prismatic crystals, m.p. 70°–71° (Straus and Lemmel), or m.p. 70°, b.p. 165°–173°/12 mm. without appreciable decomposition (von Braun, &c.); its methyl alcoholic solution becomes acidic on boiling. Willstätter and King (*l.c.*), by adding the dibromide slowly to a mixture of absolute alcohol and powdered zinc at 55°–60°, obtained pure 1:2-dihydronaphthalene, whilst Straus (*l.c.*), in repeating this experiment, obtained in addition a small quantity of a substance containing bromine. On the other

hand, von Braun and Kirschbaum (*l.c.*) showed that when treated with zinc and alcohol, *ac*-1 : 2-dibromotetrahydronaphthalene is converted into Δ^1 -dihydronaphthalene, but that the yield is never more than 80 p.c., whereas when treated with magnesium in the presence of ether, free from alcohol, pure Δ^1 -dihydronaphthalene is readily and quantitatively obtained. Moreover, the latter authors found that when similarly treated in non-hydroxylic solvents, such as benzene, ether, or acetone, a *polymeride of dihydronaphthalene*, yellow powder, m.p. 220° after softening at 212°, which appears to owe its production to the intermediate formation of organo-metallic complexes, is obtained. *bis*- Δ^1 -*Dihydronaphthalene* (or 1 : 2 : 1' : 2' - *bis*-*dihydronaphthalene*), b.p. 243°–245°/12 mm. (probably a mixture of isomerides from which on protracted cooling a *substance*, $C_{20}H_{20}$, m.p. 93°, separates) is obtained when Δ^1 -dihydronaphthalene, diluted with a hydrocarbon, *e.g.* light petroleum, benzene, xylene or tetrahydronaphthalene, is treated with concentrated sulphuric acid. The reaction products, on dehydrogenation with lead oxide, yield bisnaphthalene, a yellow powder, m.p. 165°, and on oxidation yield phthalic and phthalonic acids. When condensed with styrene, Δ^1 -dihydronaphthalene forms a *substance*, b.p. 221°–225°/22 mm. (von Braun and Kirschbaum, *l.c.*).

When *ac*-1 : 2-dibromotetrahydronaphthalene is treated with methyl alcoholic potassium hydroxide, or sodium ethylate, it yields a mixture of naphthalene and an oil with a ketonic odour, but it is scarcely affected by trimethylamine, dimethylamine or pyridine at 100°, whilst secondary and primary aromatic amines convert it into polynuclear nitrogen compounds. On the other hand, diethylamine or piperidine convert it into an apparently homogeneous *bromo*- Δ^1 -*dihydronaphthalene*, b.p. 137°/15 mm. of unknown orientation, which, on further bromination, yields a *dibromide*, leaflets, m.p. 71° (von Braun and Kirschbaum, *l.c.*). Straus and Rohrbacher, on the other hand, by heating *ac*-1 : 2-dibromotetrahydronaphthalene under diminished pressure at 130°, and finally at 175°, obtained 1-*bromo*- Δ^1 -*dihydronaphthalene*, a colourless oil, darkening on keeping, b.p. 144°–146°/17 mm., together with naphthalene and Δ^1 -dihydronaphthalene.

ac-2-*Chloro*-1-*hydroxy*-*tetrahydronaphthalene* (or Δ^1 -*dihydronaphthalene chlorohydrin*), coarse transparent needles, m.p. 92°, is prepared by the action of hypochlorous acid on Δ^1 -dihydronaphthalene (Straus and Rohrbacher, *l.c.*). The corresponding *iodohydrin* when treated in ethereal solution with silver nitrate is converted into *hydrindene-2-aldehyde*, b.p. 135°/30 mm., D_D^{20} 1.095, which yields a *semicarbazone*, m.p. 167°, an *oxime*, m.p. 104°, and a *bisulphite* compound. Neither the *iodohydrin* of *ac*-2 : 3-dihydroxytetrahydronaphthalene nor the *iodohydrin* of *hydrindene glycol* undergo a similar transformation when treated with silver nitrate (Tiffeneau and Orékhoff, *Compt. rend.* 1920, 170, 465). By treating *ac*-1 : 2-dibromotetrahydronaphthalene with water, alcohols, ketones or acids, with or without the addition of inert solvents, the α -bromo-atom is replaced by OR or O·CO·R, where R represents hydrogen, or a hydrocarbon residue, whilst the β -bromine

atom is unaffected. Moreover, physiologically active compounds of therapeutic value are prepared from these *ac*- β -bromotetrahydronaphthalene compounds, substituted in the α -position by a group containing oxygen, by treatment with ammonia, primary and secondary amines, with or without the addition of solvents. *ac*-2-*Bromo*-1-*methoxytetrahydronaphthalene*, b.p. 154°–156°/13 mm. (Straus and Rohrbacher), or b.p. 151°–152°/13 mm. (von Braun and Kirschbaum), or b.p. 159°/17 mm. (Tetralin, G.m.b.H., D. R. PP. 335476, 335477, 1919) is obtained as the sole product when *ac*-1 : 2-dibromotetrahydronaphthalene is boiled with methyl alcohol in the presence of magnesium carbonate, or with methyl alcohol alone, and as the main product together with some naphthalene and *monobromodihydronaphthalene* when boiled with $2\frac{1}{3}$ molecular proportions of 1 p.c. sodium methoxide solution for 1 hour. The following hydroxy- and alkyloxy-compounds and their amino-derivatives are obtained as indicated above.

ac-2-*Bromo*-1-*hydroxytetrahydronaphthalene* (or Δ^1 -*dihydronaphthalene bromohydrin*), long transparent needles, m.p. 111°–112°, is obtained by heating *ac*-1 : 2-dibromotetrahydronaphthalene with aqueous acetone with, or without, the addition of magnesium carbonate. The yield, when magnesium carbonate is used, is nearly quantitative and the product is nearly pure. It is also obtained by the action of hydrogen bromide on Δ^1 -dihydronaphthylene-1 : 2-oxide. The bromohydrin yields *ac*-2-*amino*-1-*hydroxytetrahydronaphthalene*, m.p. 112°; *ac*-2-*diethylamino*-1-*hydroxytetrahydronaphthalene*, colourless, rather viscous liquid, b.p. 170°/10 mm. (Tetralin, G.m.b.H.), or b.p. 166°–167°/12–13 mm. (Straus and Rohrbacher, *Ber.* 1921, 54, 40); *ac*-2-*methylamino*-1-*hydroxytetrahydronaphthalene*, colourless viscous oil, b.p. 164°–166°/12–13 mm. (Straus and Rohrbacher), or 168°–169°/10 mm. (Tetralin, G.m.b.H.), *hydrochloride*, m.p. 183°–184°, after softening at 179°; *ac*-2-*dimethylamino*-1-*hydroxytetrahydronaphthalene*, b.p. 157°–158°/10 mm. (Tetralin, G.m.b.H.), or 170°–171°/20 mm. (Straus and Rohrbacher), *hydrochloride*, prismatic needles, m.p. 173°–175°; *ac*-2-*piperidino*-1-*hydroxytetrahydronaphthalene*, m.p. 72°–73°, *hydrochloride*, rods, m.p. 182°–183°, *aurichloride*, long yellow needles, m.p. 167°–168° (decomp.), *platinichloride*, small needles, m.p. 186°–188° (decomp.), *picrate*, long yellow rods, m.p. 147.5°–148.5°, *benzoyl derivative*, square prisms, m.p. 81°.

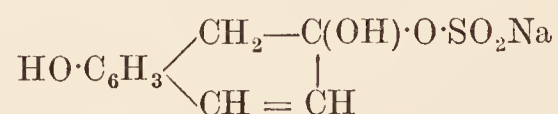
Δ^1 -Dihydronaphthalene, when treated with bromotrinitromethane in methyl alcoholic solution, yields a *bromomethoxytetrahydronaphthalene*, colourless liquid, b.p. 101°/0.31 mm. (Schmidt, Bartholomé and Lübke, *Ber.* 1922, 55, 2099).

ac-2-*Bromo*-1-*ethoxytetrahydronaphthalene*, b.p. 163°–165°/20 mm. (Tetralin, G.m.b.H.), or b.p. 171°–172°/21 mm. (von Braun and Kirschbaum), yields *ac*-2-*dimethylamino*-1-*ethoxytetrahydronaphthalene*, b.p. 152°/13 mm., *hydrochloride*, oil, *picrate*, m.p. 199°, *methiodide*, m.p. 166°; *ac*-2-*piperidino*-1-*ethoxytetrahydronaphthalene*, b.p. 170°/11 mm.; *ac*-2-*diethylamino*-1-*allyloxytetrahydronaphthalene*, b.p. 165°/10 mm. *ac*-2-*Bromo*-1-*amyloxytetrahydronaphthalene* boils at 175°–180°/15 mm. *ac*-2-*Bromo*-1-*acetoxytetrahydronaphthalene*, m.p. 94° (Tetralin, G.m.b.H.), or 95°–96°

(von Braun and Kirschbaum) is formed by the limited action of potassium acetate and glacial acetic acid on ac-1:2-dibromotetrahydronaphthalene, whereas by prolonged action both bromine atoms may be replaced by acetoxy-groups. On hydrolysis with alcohol and fuming hydrochloric acid at 50°–60° ac-2-bromo-1-acetoxytetrahydronaphthalene yields ac-2-bromo-1-hydroxytetrahydronaphthalene, whilst ac-2-dimethylamino-1-acetoxytetrahydronaphthalene similarly yields ac-2-dimethylamino-1-hydroxytetrahydronaphthalene. ac-2-Bromo-1-allyloxytetrahydronaphthalene boils at 171°/11 mm.; dibromide, an oil (Straus and Rohrbacher, Ber. 1921, 54, 40; von Braun and Kirschbaum, *ibid.* 597; Tetralin, G.m.b.H., D. R. PP. 335476, 335477, 1919). Some of the above compounds and further derivatives of this type are described by von Braun, Braunsdorf and Kirschbaum (Ber. 1922, 55, 3648). ac-2-Bromo-1-hydroxytetrahydronaphthalene is converted by dry hydrogen bromide into ac-1:2-dibromotetrahydronaphthalene, and is reduced by zinc-dust and alcohol, or amalgamated aluminium, to Δ^1 -dihydronaphthalene, whilst on treatment with sodium in moist ethereal solution the bromohydrin is converted into a mixture of Δ^1 -dihydronaphthalene and ac-tetrahydro- β -naphthol, b.p. 139°–140°/12 mm., with the intermediate formation of the ethylene oxide. On oxidation with sodium bichromate and sulphuric acid, the bromohydrin yields ac-2-bromo-1-ketotetrahydronaphthalene, pale yellow oil with a characteristic and very unpleasant odour, b.p. 140°–142°/0.5–1 mm.; oxime, colourless needles, m.p. 136.5°–137°. ac-2-Bromo-1-ketotetrahydronaphthalene on reduction with zinc dust and alcohol yields ac-1-ketotetrahydronaphthalene, which is identical with the product obtained in 10 p.c. yield by Kipping and Hill (Chem. Soc. Trans. 1899, 75, 144) by the action of aluminium chloride on phenylbutyryl chloride in light petroleum solution (b.p. 100°–110°). Schroeter (Annalen, 1922, 426, 88; Schroeter and Tetralin, G.m.b.H., D. R. P. 352720, 1920) showed that ac-1-ketotetrahydronaphthalene (α -tetralon) is formed to the extent of about 10 p.c., together with ar-tetrahydro- α -naphthol and tetrahydronaphthalene by the cautious or incomplete reduction of α -naphthol with hydrogen in presence of a nickel catalyst; or, in a yield of about 50 p.c. by the action of concentrated sulphuric acid at 100° on γ -phenyl-*n*-butyric acid (Krollpfeiffer and Schäfer, Ber. 1923, 56, 620). ac-1-Ketotetrahydronaphthalene is a colourless mobile refractive oil with a faint odour recalling that of camphor when cold, and of peppermint when warmed, b.p. 132°–133°/13 mm., or b.p. 127°/13 mm. (Krollpfeiffer and Schäfer, *l.c.*). It is readily volatile with steam and does not form a bisulphite compound; benzylidene derivative, m.p. 206°–207° (Wallach and Weissenborn, Annalen, 1924, 437, 148); semicarbazone, long transparent yellow needles or prisms, m.p. 217°–220°, from which the pure ketone is obtained by hydrolysis with warm hydrochloric acid; phenylhydrazone, massive transparent rhomboidal plates, m.p. 84°–85°, is very unstable; p-bromophenylhydrazone, long colourless prisms or massive transparent crystals, m.p. 117°–118°; oxime, lustrous rhomboidal crystals, m.p. 102.5°–103.5°, separated

by steam distillation into a more volatile isomeride, colourless needles, m.p. 88°–89°, and a less volatile, large colourless prisms, m.p. 102°–103°. The former is converted into the latter by the Beckmann rearrangement, whereas the latter gives a nitrile-like liquid and another isomeride, colourless needles or prisms, m.p. 134°–136° (Inoue, J. Soc. Chem. Ind. Japan, 1923, 26, 1335). The oxime of ac-1-ketotetrahydronaphthalene on reduction with sodium amalgam in warm dilute acetic acid solution yields ac-tetrahydro- α -naphthylamine, whilst when the ketone is reduced with sodium in boiling absolute alcoholic solution, ac-tetrahydro- α -naphthol is formed. The chlorination of ac-1-ketotetrahydronaphthalene gives monochloro-1-ketotetrahydronaphthalene, m.p. 45°, and dichloro-1-ketotetrahydronaphthalene, m.p. 75°–76° (Tetralin, G.m.b.H. and Riebenschahm, D. R. P. 377587). When the calculated quantity of methyl alcoholic potassium hydroxide is added gradually to a solution of ac-2-bromo-1-hydroxytetrahydronaphthalene in absolute alcohol, it yields Δ^1 -dihydronaphthalene oxide, or ac-tetrahydronaphthylene-1:2-oxide, a transparent mobile liquid with a pronounced odour of naphthalene, b.p. 86°–88°/1–2 mm., or 76°–78°/0 mm., which crystallises in large leaflets, m.p. 20°–21°. It is also obtained, b.p. 114°–116°/10 mm., when the methiodide of ac-2-dimethylamino-1-hydroxytetrahydronaphthalene is treated with silver oxide and heated (von Braun, Braunsdorf and Kirschbaum, *l.c.*). It is readily volatile with steam, and when distilled in the vacuum of a water pump readily polymerises with the formation of a substance, white amorphous flocks, m.p. about 136°–137°, with discoloration and evolution of gas. 5-Hydroxy-ac-1-ketotetrahydronaphthalene, colourless crystals, m.p. 156°–157° (semicarbazone, m.p. 224°), 8-hydroxy-ac-1-ketotetrahydronaphthalene, and 5-acetylamino-ac-1-ketotetrahydronaphthalene, are obtained from 1:5-dihydroxynaphthalene, 1:8-dihydroxynaphthalene, and 1-hydroxy-5-acetylamino-naphthalene, respectively, by reduction with hydrogen under pressure in presence of reduced nickel deposited on kieselguhr (Schroeter and Tetralin, G.m.b.H., D. R. P. 352720, 1920).

Sodium 5-hydroxy-ac-1-ketotetrahydronaphthalene 3-sulphonate is obtained by treating the sodium salt, $C_{10}H_{10}O_3S_2Na_2$ (produced by the prolonged action of sodium hydrogen sulphite on 1:5-dihydroxynaphthalene), with alkali hydroxide or boiling water. It forms a phenylhydrazone, $C_{16}H_{16}O_4N_2S$, and on treatment with diazomethane, is converted into sodium 5-methoxy-ac-1-ketotetrahydronaphthalene 3-sulphonate. 2:7-Dihydroxynaphthalene, under analogous conditions, reacts with sodium hydrogen sulphite in a different manner, forming a substance, $C_{10}H_9O_5SNa$, apparently



in only 20 p.c. yield (Fuchs and Stix, Ber. 1922, 55, 658). When ac-2-bromo-1-hydroxytetrahydronaphthalene is treated with aqueous alkalis, ac-cis-trans-1:2-dihydroxytetrahydronaphthalene, long colourless needles, m.p. 112°–113°, is obtained, the ethylene oxide probably being

formed as an intermediate product; *diacetate*, transparent pointed prisms, m.p. 84° , from which the glycol is regenerated quantitatively on hydrolysis with methyl alcoholic potassium hydroxide solution. When, however, *ac-1:2-dibromotetrahydronaphthalene* is treated with glacial acetic acid and potassium acetate, a mixture of the acetates of the two stereoisomeric glycols is obtained, and their separation is effected mechanically after crystallisation from light petroleum. The *cis-acetate* forms long colourless coarse prisms, m.p. 78.6° – 79.2° , from which the *cis-glycol* is obtained by hydrolysis, and crystallises in leaflets, m.p. 101.5° – 102° . The action of mercuric acetate on Δ^1 -dihydronaphthalene also yields a mixture of the stereoisomeric glycols (Straus and Rohrbacher, *l.c.*).

ac-2-Bromo-1-ethoxy-tetrahydronaphthalene on treatment with magnesium yields primarily a mixture of *ac-1-ethoxy-tetrahydronaphthalene* and *ac-1:1'-diethoxy-2:2'-bis-tetrahydronaphthalene*, neither of which could be obtained pure on account of the ready elimination of ethyl alcohol with the formation of Δ^1 -dihydronaphthalene and $\beta\beta'$ -*bis- Δ^1 -dihydronaphthalene*, colourless leaflets, m.p. 156° , respectively. The latter compound on reduction with sodium and ethyl alcohol yields $\beta\beta'$ -*bis-tetrahydronaphthalene*, colourless leaflets, m.p. 113° , from which $\beta\beta'$ -dinaphthyl is obtained by distillation with lead oxide. The latter compound is also formed readily by the bromination of $\beta\beta'$ -*bis- Δ^1 -dihydronaphthalene*, as the tetrabromide, which is formed first, readily loses hydrogen bromide (von Braun and Kirschbaum, *Ber.* 1921, 54, 597). *ac-1-Keto-2-methyl-tetrahydronaphthalene*, b.p. 127° – $131^{\circ}/12$ mm., or b.p. $132^{\circ}/15$ mm., d_4^{20} 1.061, n_D^{20} 1.552 (*semicarbazone*, colourless leaflets, m.p. 199° – 201° when heated rapidly) (Krollpfeiffer and Schäfer, *Ber.* 1923, 56, 620), is formed by the action of aluminium chloride on γ -phenyl- α -methylbutyryl chloride dissolved in light petroleum (b.p. 60° – 70°). It is converted by ethereal magnesium methyl-iodide into *ac-1-hydroxy-1:2-dimethyltetrahydronaphthalene*, m.p. 64° – 66° , b.p. 135° – $140^{\circ}/15$ mm., which on heating to 160° – 180° yields *ac-1:2-dimethyl- Δ^1 -dihydronaphthalene*, b.p. 114° – $116^{\circ}/15$ mm. or 250° – $251^{\circ}/\text{atm.}$, D^{17} 0.9885, n_D 1.5763. The latter compound forms a *dibromide*, pale yellow oil, which is converted by boiling methyl alcoholic potassium hydroxide into *ac-2-methyl-1-methylene- Δ^2 -dihydronaphthalene*, b.p. $157^{\circ}/15$ mm., which yields 1:2-dimethylnaphthalene on boiling with glacial acetic acid containing hydrogen chloride (Schroeter, Lichtenstadt and Irineu, *Ber.* 1918, 51, 1600).

7 - *Methyl-ac-1-ketotetrahydronaphthalene*, colourless crystalline aggregates, m.p. 32.5° – 33.5° , d_4^{20} 1.072, n_D^{20} 1.563 (*semicarbazone*, colourless slender needles, m.p. 224° – 225°), is obtained by the action of concentrated sulphuric acid on γ -*p*-tolyl-*n*-butyric acid. On treatment with bromine in carbon disulphide solution it forms 7-*methyl-ac-1-keto-2-bromotetrahydronaphthalene*, slender colourless needles, m.p. 80.5° , converted by boiling diethylaniline into 7-*methyl-ac-1-ketotetrahydronaphthalene* and 7-*methyl- α -naphthol*, colourless needles, m.p. 109° .

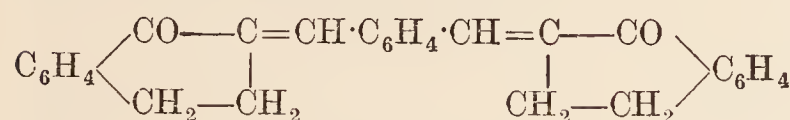
7-*Ethyl-ac-1-ketotetrahydronaphthalene*, colourless oil, b.p. 152° – $153^{\circ}/12$ mm., d_4^{20} 1.053, n_D^{20} 1.559 (*semicarbazone*, colourless needles, m.p. 223° – 225°), 5:7-*dimethyl-ac-1-ketotetrahydronaphthalene*, coarse prisms, m.p. 49° – 50° , d_4^{20} 1.061, n_D^{20} 1.563 (*semicarbazone*, slender colourless needles, m.p. 234° – 235°), and 7-*methoxy-ac-1-ketotetrahydronaphthalene*, colourless plates, m.p. 60° – 61° (*semicarbazone*, m.p. 222° – 224° when heated rapidly), are obtained from γ -*p*-ethylphenyl-*n*-butyric acid, γ -*m*-xylyl-*n*-butyric acid, or preferably the acid chloride, and γ -*p*-methoxyphenyl-*n*-butyryl chloride, respectively, either by the action of concentrated sulphuric acid, or, if the products are sulphonated readily, by means of aluminium chloride (Krollpfeiffer and Schäfer, *l.c.*).

ac-1-Keto-2:3-dimethyltetrahydronaphthalene, b.p. 148° – $150^{\circ}/17$ mm., m.p. -1° , D^{21} 1.019, is formed when γ -phenyl- $\alpha\beta$ -dimethyl-butyl chloride is treated in a similar manner to that used in the preparation of the monomethyl analogue. On reduction with sodium and alcohol it forms *ac-2:3-dimethyltetrahydro- α -naphthol*, m.p. 110° – 114° , b.p. 148° – $152^{\circ}/18$ mm., which loses water at 200° and produces *ac-2:3-dimethyl- Δ^1 -dihydronaphthalene*, b.p. 120° – $140^{\circ}/16$ mm. The *dibromide* of the latter compound, on treatment with boiling methyl alcoholic potassium hydroxide, is converted into 2:3-dimethylnaphthalene, identical with guaiane (Schroeter, Lichtenstadt and Irineu, *Ber.* 1918, 51, 1600). When γ -methylene-dioxy-phenyl-butyl chloride, m.p. 83° , is treated with phosphorus trichloride, and the product distilled, *ar-methylene-dioxy-ac- α -keto-tetrahydronaphthalene*, colourless needles, m.p. 77° – 78° , b.p. $191^{\circ}/18$ mm. is obtained; *semicarbazone*, crystalline powder, m.p. 258° (decomp.) (Borsche and Eberlein, *Ber.* 1914, 47, 1466).

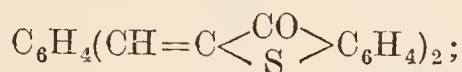
ac-1-Ketotetrahydronaphthalene condenses readily with isatin in aqueous alcoholic potassium hydroxide solution forming 5:6-*dihydro- α -naphthacridine-7-carboxylic acid*, slender, pale yellow needles, m.p. 252° (decomp.), which readily undergoes further change and which forms salts decomposed by water. The *ethyl-ester* melts at 80° . The acid when heated a little above its melting-point yields 5:6-*dihydronaphthacridine*, m.p. 60° , b.p. 237° – $238^{\circ}/10$ mm., and is converted by bromine in glacial acetic acid solution at 120° – 130° into α -naphthacridine 7-carboxylic acid, yellow powder, m.p. 261° , whilst, on treatment with sodium and ethyl or amyl alcohol, it yields 5:6:6a:7:12:12a-*hexahydro- α -naphthacridine 7-carboxylic acid*, m.p. 190° (decomp.) after softening at 180° . *ac-1-Ketotetrahydronaphthalene* condenses in a similar manner with *o*-methylisatin, yielding 5:6-*dihydro-11-methyl- α -naphthacridine 7-carboxylic acid*, m.p. 188° (decomp.) (von Braun and Wolff, *Ber.* 1922, 55, 3675); whilst when heated with an equivalent quantity of α -isatinanil in petroleum (b.p. 150° – 200°) it yields 2-*tetrahydronaphthalene-2'-indole-indigotin*, bluish-violet crystals with a bronze reflex, decomposing at about 250° and converted by fuming sulphuric acid into a *sulphonic acid*. When treated with α -thionaphthenquinoneanil in boiling acetic anhydride solution, the ketone gives rise to 1-*keto-2:3'-oxy-2'-thionaphthen-*

tetrahydronaphthalene, reddish-violet needles, decomposing about 250°. On sulphonation this yields a *sulphonic acid*.

The ketone also reacts with terephthalaldehyde in alcoholic solution in presence of sodium hydroxide forming the *compound*

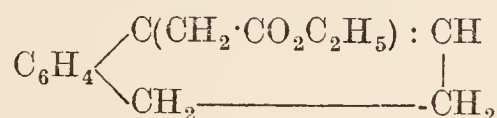


straw-yellow crystals, m.p. 240°–255° after darkening at 230°; with terephthalaldehyde and 3-hydroxythionaphthen yielding mainly a *substance*, golden-yellow needles, m.p. 192°, and a small amount of the dye



with cinnamaldehyde yielding *β-cinnamylidene-α-ketotetrahydronaphthalene*, large yellow leaflets, m.p. 132°–134°, which is polymerised at 220°–230° (Herzog and Kreidl, Ber. 1922, 55, 3394).

ac-1-Ketotetrahydronaphthalene condenses with zinc and ethyl bromoacetate to form the unsaturated *ester*



b.p. 183°–184°/16 mm., which on hydrolysis yields the *acid*, colourless needles, m.p. 110°. This latter compound is slowly hydrogenated in presence of palladium chloride to *ac-1-tetrahydronaphthylacetic acid*, m.p. 35°–36°, which is converted through the amide into *ac-tetrahydro-α-naphthylmethylamine*, but in small yield (von Braun, Gruber and Kirschbaum, Ber. 1922, 55, 3664).

By the action of concentrated sulphuric acid on *β-benzylglutaric acid*, *benzyl-succinic acid* (or its anhydride), and *benzylethane tricarboxylic acid*, *ac-1-ketotetrahydronaphthalene-3-acetic acid*, prisms, sintering at 109° and melting at 110°–111° (*semicarbazone*, crystalline powder, m.p. 238°), *ac-1-ketotetrahydronaphthalene-3-carboxylic acid*, flocculent precipitate, m.p. 149° (*semicarbazone*, crystalline powder decomposing at 261°, shrinking at 255°), and *ac-1-keto-tetrahydronaphthalene-3:3-dicarboxylic acid*, fine needles, m.p. 170°, with violent decomposition (*semicarbazone*, decomposing at 250°, darkening at 240°), are formed respectively. The 3-carboxylic acid is also obtained by heating *ac-1-keto-tetrahydronaphthalene-3:3-dicarboxylic acid* above its melting-point (Stevenson and Thorpe, Chem. Soc. Trans. 1922, 121, 1717; Attwood, Stevenson and Thorpe, *ibid.* 1923, 123, 1755).

ar-5:8-Dihydro-α-naphthylamine, colourless rhombic plates or needles, m.p. 37·5°, b.p. 247°/408 mm., is formed together with its 7:8- or 5:6-isomeride by the regulated reduction of *α-naphthylamine* with sodium and absolute ethyl alcohol in the presence of solvent naphtha (b.p. 139°); the reduction product is purified by conversion into the *benzylidene derivative*, massive rhombic prisms, m.p. 69°, followed by hydrolysis with hydrochloric acid. The amine forms a *hydrochloride*, stout colourless needles; *acetyl derivative*, colourless silky needles, m.p. 163°; 2:4-*dinitro-phenyl derivative*, reddish-brown rhombic plates, m.p. 144°. When

ar-5:8-dihydro-α-naphthylamine is diazotised and treated with an alkaline sodium stannite solution 1:4-dihydronaphthalene is obtained. *ar-7:8- or 5:6-Dihydro-α-naphthylamine*, colourless oil, b.p. 180°–182°/30 mm., is prepared from *ar-5:8-dihydro-α-naphthylamine* by heating with sodium ethoxide at 140° for 1 hour; *hydrochloride*, straw-coloured feathery needles; *benzylidene derivative*, long crystals which are a combination of a rhombic prism and pyramid, m.p. 64°; *acetyl derivative*, silky needles, m.p. 153°; 2:4-*dinitrophenyl derivative*, reddish-brown leaflets or needles, m.p. 136°. When the amino-group is removed 1:2-dihydronaphthalene is obtained, and, on further treatment with sodium and ethyl alcohol, the amine is converted into *ar-tetrahydro-α-naphthylamine* (Rowe and Levin, Chem. Soc. Trans. 1920, 117, 1574).

5:8- and 7:8-Dihydro-α-naphthylamine on oxidation with acid dichromate yield *α-naphthoquinone* together with traces of phthalic acid, whilst with alkaline permanganate the former is destructively oxidised.

4-Bromo:5:8-dihydroaceto-α-naphthalide, forms flat silvery needles, m.p. 213·5°, with previous softening; 6:7-dibromotetrahydroaceto-α-naphthalide, silky feathery needles, m.p. 179°–179·5°; 4:6:7-tribromotetrahydroaceto-α-naphthalide, well-defined colourless needles, m.p. 201·5°–202° (Rowe and Davies, Chem. Soc. Trans. 1922, 121, 1000).

ar-5:8-Dihydro-α-naphthol, colourless plates or needles, m.p. 75°, is not obtained conveniently by the direct hydrogenation of *α-naphthol* by means of sodium and ethyl alcohol, but it can be obtained from *ar-5:8-dihydro-α-naphthylamine* by the diazo-reaction. On sulphonation it yields *ar-5:8-dihydro-α-naphthol-4-sulphonic acid*, which does not couple with diazonium salts to form azo-dyes, and which regenerates the dihydronaphthol on hydrolysis with dilute acids. *ar-2-Nitro-5:8-dihydro-α-naphthol*, yellow needles, m.p. 98°, is obtained by the action of nitric acid on a solution of the sulphonic acid in sulphuric acid, followed by hydrolysis of the nitrosulphonic acid. It couples with diazonium salts to form azo-dyes. *ar-2:4-Dinitro-5:8-dihydro-α-naphthol*, long yellow prismatic needles, m.p. 127°, is obtained by the dinitration of *ar-5:8-dihydro-α-naphthol-4-sulphonic acid*.

ar-7:8- or 5:6-Dihydro-α-naphthol, silky plates or needles, m.p. 71°, is obtained from the corresponding amine by the diazo-reaction, or from *α-naphthol* by the action of sodium and ethyl alcohol in the presence of toluene or solvent naphtha (b.p. 139°). On further treatment with sodium and ethyl alcohol it is converted into *ar-tetrahydro-α-naphthol*.

ar-2-Nitro-7:8- or 5:6-dihydro-α-naphthol, yellow needles, m.p. 55°, is formed by the nitration of *ar-7:8- or 5:6-dihydro-α-naphthol-4-sulphonic acid* (Rowe and Levin, Chem. Soc. Trans. 1921, 119, 2021).

Two of the three possible dihydro-α-naphthoic acids, containing the unsaturated linking in the same ring as the carboxyl group, have been isolated (von Sowinski, Ber. 1891, 24, 2354; Baeyer, Schoder and Besemfelder, Annalen, 1891, 266, 169; Kamm and McClugage, J. Amer. Chem. Soc. 1916, 38, 419).

Labile Δ²-dihydro-α-naphthoic acid (or *ac-*

1:4-dihydro- α -naphthoic acid) is formed by reducing α -naphthoic acid with sodium amalgam at low temperatures. It crystallises in colourless monoclinic needles, m.p. 91° (Baeyer, &c.), or 86.5° (Kamm and McClugage), or 76° (von Sowinski). It forms a *dibromide*, crystalline powder, m.p. 132° (Baeyer, &c.), or 125° (Kamm and McClugage), which, on treatment with 5 p.c. potassium hydroxide solution, yields α -naphthoic acid and a little naphthalene, whilst on treatment with zinc and glacial acetic acid it is converted readily into the original dihydro- α -naphthoic acid. According to von Sowinski the dibromide is unstable, and on treatment with cold aqueous sodium carbonate it is converted into a monobromohydronaphthoic acid. *Stable* or *ac-3:4-dihydro- α -naphthoic acid* is formed by boiling the labile acid for a few hours with sodium hydroxide or by the reduction of α -naphthoic acid with sodium amalgam at the ordinary temperature without cooling. It forms monoclinic crystals, m.p. 125° (Baeyer, &c.), or 112° (von Sowinski), or 121.5° (Kamm and McClugage), or 110° – 120° (Rabe, Ber. 1898, 31, 1899), and yields a *dibromide*, m.p. 152° (Baeyer, &c.), or 151° (decomp.) (Kamm and McClugage), or 136° (decomp.) (von Sowinski). The dibromide, on treatment with 5 p.c. potassium hydroxide, yields a coloured acidic substance, and *ac-1:2-dihydroxy-tetrahydronaphthoic acid*, white plates, m.p. 175° (Kamm and McClugage), whereas methyl alcoholic potassium hydroxide converts it into α -naphthoic acid and dihydro- α -naphthoic acid, and treatment with zinc-dust and glacial acetic acid regenerates the *ac-3:4-dihydro- α -naphthoic acid*. The attempted isolation of the third *ac*-dihydro- α -naphthoic acid, involving the reduction of 4-ethoxy- α -naphthoic acid without loss of the ethoxy-group, failed.

The three possible dihydro- β -naphthoic acids, containing the added hydrogen atoms in the same ring as the carboxyl group, have been isolated (von Sowinski, *l.c.*; Baeyer, Schoder and Besemfelder, *l.c.*; Derick and Kamm, J. Amer. Chem. Soc. 1916, 38, 400).

When β -naphthoic acid is reduced with sodium amalgam a mixture of labile *ac-1:2-dihydro- β -naphthoic acid* and the more stable *ac-1:4-dihydro- β -naphthoic acid* is formed. *Labile* or *ac-1:2-dihydro- β -naphthoic acid*, prisms, m.p. 104° – 105° (Baeyer, &c.), or 103° (von Sowinski), or 101.2° (Derick and Kamm), forms an unstable *dibromide*, which decomposes spontaneously into the lactone of an *ac-bromo-tetrahydro- β -naphthoic acid*, monoclinic crystals, m.p. 124° (decomp.), which regenerates the labile acid on treatment with zinc and glacial acetic acid, whilst, with alcoholic potash, β -naphthoic acid is obtained (von Sowinski; Baeyer, &c.). On the other hand, the dibromide, *ac-3:4-dibromotetrahydro- β -naphthoic acid*, m.p. 172° (decomp.), which Derick and Kamm obtained from the labile *ac-1:2-dihydro- β -naphthoic acid* was not found to be liable to undergo spontaneous decomposition. Hosaeus (Ber. 1893, 26, 670) obtained a substance, needles, m.p. 160° , which he considered to be α -naphthoic acid by the action of sodium amalgam on 2:3-chloronaphthoic acid, but Gradenwitz (Ber. 1894, 27, 2622) showed it to be *ac-1:4-dihydro- β -naphthoic acid*.

Stable or *ac-1:4-dihydro- β -naphthoic acid*, colourless nacreous plates, m.p. 161° (Derick and Kamm), or 158° (von Sowinski), is obtained readily from the labile acid by treatment with sodium hydroxide, but the conversion is never complete and, in the presence of air, β -naphthoic acid also is formed. It is prepared more conveniently by boiling a solution of the potassium salt of β -naphthoic acid with 3 p.c. sodium amalgam until the whole of the β -naphthoic acid has been reduced, followed by fractional precipitation of an ammoniacal solution with hydrochloric acid. It forms a *dibromide*, monoclinic crystals, m.p. 208° , which with alcoholic potash yields β -naphthoic acid, whilst zinc-dust and glacial acetic acid apparently regenerate the original dihydro- β -naphthoic acid. *ac-3:4-Dihydro- β -naphthoic acid*, clusters of radiating needles, m.p. 118° , is formed by boiling either the 1:4- or the 1:2-isomeride with barium hydroxide under pressure or with potassium hydroxide; *ac-1:2-dibromotetrahydro- β -naphthoic acid*, white crystals, m.p. 190° (decomp.).

The monobromo-lactone derived from the labile *ac-1:2-dihydro- β -naphthoic acid*, when boiled with 20 p.c. potassium hydroxide solution, yields *ac-4-ketotetrahydro- β -naphthoic acid*, m.p. 143° – 145° ; *semicarbazone*, m.p. 266° (decomp.).

ac-1:2-Dibromotetrahydro- β -naphthoic acid yields *ac-1:2-dihydroxytetrahydro- β -naphthoic acid*, white plates, m.p. 182° , which is oxidised by alkaline permanganate to *o*-carboxy- β -phenyl-propionic acid, whilst *ac-3:4-dihydro- β -naphthoic acid* when similarly oxidised yields first a product which is apparently the hydrate of *ac-2-hydroxy-1-ketotetrahydro- β -naphthoic acid*, m.p. 119° – 120° , and on further oxidation gives *o*-carboxy- β -phenyl-propionic acid and phthalic acid (Derick and Kamm, *l.c.*).

By allowing a mixture of benzyl acetoacetate and slightly diluted sulphuric acid to stand for several hours, von Pechmann (Ber. 1883, 16, 516) obtained a product which possessed the properties of a dihydronaphthoic acid, but which was considered by Roser (Ber. 1887, 20, 1575) to be methylindonaphthene carboxylic acid.

Ethyl Δ^1 -dihydro- α -naphthoate is a liquid possessing a characteristic odour, b.p. 305° – $306^\circ/748$ mm. The ester when heated for 48 hours with alcoholic sodium ethoxide and ethyl acetoacetate is converted into ethyl diketo-octahydrophenanthrene carboxylate (Rabe, Ber. 1898, 31, 1899).

Menthyl Δ^1 -dihydro- α -naphthoate is a resinous substance, b.p. 226° – $227.5^\circ/12$ mm., $[\alpha]_D = -69.12^\circ$; *menthyl Δ^2 -dihydro- α -naphthoate*, colourless prisms, m.p. 89° – 89.5° , $[\alpha]_D = +92.85^\circ$ (Rupe, Lotz and Silberberg, Annalen, 1903, 327, 157).

Menthyl Δ^2 -dihydro- β -naphthoate, colourless viscid oil, b.p. $218^\circ/10.5$ mm., $[\alpha]_D^{20} = -41.40^\circ$ (benzene); *menthyl Δ^3 -dihydro- β -naphthoate* is an oil, which decomposes when heated, $[\alpha]_D^{20} = -53.14^\circ$ (benzene) (Rupe and Munter, Annalen, 1910, 373, 121).

Ethyl Δ^2 -dihydro- β -naphthoate condenses with ethyl acetoacetate in the presence of sodium ethoxide to form ethyl 2:4-diketo-octahydro-anthracene 1-carboxylate, which when hydro-

lysed gives the free acid (Colver and Noyes, J. Amer. Chem. Soc. 1921, 43, 898).

On reduction with sodium amalgam naphthalic acid is converted into a dihydronaphthalic acid together with a second reduction product. *Dihydronaphthalic acid* is a crystalline compound, which turns yellow at 150°–160° and decomposes at 199° with evolution of carbon dioxide and elimination of water. Its alcoholic solution decolorises bromine and its alkaline solution reduces permanganate solution in the cold (Anselm, Ber. 1889, 22, 859).

Tetrahydronaphthalene is formed by heating naphthalene with hydriodic acid at 280° (Berthelot), and by heating naphthalene with phosphonium iodide at 170°–180° (Baeyer). According to Baly and Tuck (Chem. Soc. Trans. 1908, 93, 1905), however, the tetrahydronaphthalene obtained by the use of phosphorus and hydriodic acid is the 1:4:5:8-compound, whereas the tetrahydronaphthalene obtained by all other methods is the 1:2:3:4-compound.

α - or 1:4:5:8-*Tetrahydronaphthalene* is an oil, b.p. 206°, sp.gr. 0.981 at 12.5°. It does not form a picrate and is oxidised by acid permanganate or by dilute nitric acid to phthalic acid (Graebe, Ber. 1872, 5, 677; Graebe and Guye, Ber. 1883, 16, 3028). Reference has already been made in the review of the methods available for the production of hydro-derivatives of naphthalene (pages 749, 750) to other reactions which yield tetrahydronaphthalene. Tetrahydronaphthalene is prepared conveniently in the laboratory by the action of sodium and amyl alcohol on naphthalene (Bamberger and Kitschelt, Ber. 1890, 23, 1561), and the product is identical with that obtained from *ar*-tetrahydro- α -naphthylamine by the diazo-reaction (Bamberger and Bordt, Ber. 1889, 22, 631). A tetrahydronaphthalene, b.p. 193°–206°, has been isolated in a series of experiments on pyrogenic acetylene condensations (Meyer and Fricke, Ber. 1914, 47, 2765).

Numerous methods have been proposed for the purification of naphthalene, in order to render it suitable for direct hydrogenation in presence of a catalyst. In the earlier stages of the development of the process, it was proposed to carry out the purification in the vapour phase in contact with finely-divided metals, fused sodium, fuller's earth, &c. Alternatively, crude naphthalene, dissolved in benzene, petroleum, tetrahydronaphthalene, &c., was purified by similar means at temperatures above 100° (Tetralin, G.m.b.H., D. R. PP. 299012, 299013, 305104, 1916). According to subsequent patents (*ibid.* D. R. PP. 324861, 1915; 324862, 1915; 324863, 1916) molten naphthalene was treated with 5–10 p.c. of a porous material, such as fuller's earth, kieselguhr, decolorising charcoal, &c., at about 150° until a sample gave no red colour when triturated with sulphuric acid. In place of, or in addition to, the porous substance, finely-divided metals, such as nickel, and readily fusible metals, such as sodium, may be used. Crude naphthalene can be purified in 1 hour, for example, by treatment with hydrogen under pressure in presence of 1 p.c. of finely-divided nickel and 0.75 p.c. of sodium at 180°. Non-acidic compounds of metals, such as sodamide, or aluminium or calcium carbide, are effective

alternative purifying agents if 1 p.c. of the compound is used at 150° for 3 hours. The purified naphthalene is filtered, or preferably distilled into the hydrogenation autoclave. The preparation of a suitable nickel catalyst electrolytically, the purification of commercial naphthalene by distillation with Japanese acid clay, and the hydrogenation of the product to tetrahydronaphthalene under 30 atmospheres pressure have been described by Inoue (J. Chem. Ind. Japan, 1923, 26, 1316). Processes have been proposed for the hydrogenation of naphthalene in the vapour phase, but do not appear to have found technical application, thus (Akt-Ges. für Anilin Fabrik. D. R. PP. 298541, 298553, 301275, 1916) a mixture of naphthalene vapour and hydrogen is passed over a suitable catalyst at 150°–200° under atmospheric pressure. A mixture of metallic oxides is used as the catalyst, for example, 2 parts manganese, 1 part copper, and 1 part nickel oxides is suitable for the hydrogenation of naphthalene to the tetrahydro-derivative at 160°–180°.

Technically, tetrahydronaphthalene (Tetralin) is prepared by the process of the Tetralin, G.m.b.H. from naphthalene purified by the processes already indicated. The hydrogenation is effected in an autoclave, capable of resisting 40 atmospheres pressure, fitted with an agitator, an arrangement for distilling the reaction product under diminished pressure, and an arrangement for the introduction of fresh charges of naphthalene. As many as 20–40 hydrogenations can be effected in such an apparatus without opening it or renewing the catalyst. The hydrogenation is an exothermic process, so that heat is only necessary on the large scale to commence the reaction (*cf.* Leroux, Compt. rend. 1910, 151, 382; Roth and von Auwers, Annalen, 1915, 407, 174). The arrival at the tetrahydro-stage is readily recognised owing to a diminution in the rate of absorption of hydrogen.

The process for the production of Tetralin has been described by Schroeter and collaborators (Annalen, 1922, 426, 13). 512 grms. of naphthalene, purified as already indicated and distilled *in vacuô*, are placed in an autoclave together with 15–20 grms. of a suitable compound containing nickel. The naphthalene is melted and the autoclave is closed by a cover fitted with an agitator, thermometer tube, manometer, a tube for the introduction of hydrogen, and a delivery tube. Pure hydrogen is introduced until a pressure of 12–15 atmospheres is reached, agitation is commenced, and the temperature raised to 180°–200°. At this temperature, the pressure falls at the rate of about 1 atmosphere per minute, and if it falls to 8–5 atmospheres, hydrogen is introduced to raise the pressure to 12–15 atmospheres again, until the sum of the decreases in pressure is equivalent to an absorption of two molecular proportions of hydrogen, *i.e.* 178 litres at 0°/760 mm. Towards the end of the reaction it is advisable to cease the further introduction of hydrogen, so that the hydrogen in the autoclave may be absorbed almost completely, which is the case after a few minutes. The conversion of the naphthalene into Tetralin requires from 1 to 1½ hours. The delivery tube is connected to a condenser and a vacuum pump, the contents of the autoclave are stirred slowly, and the Tetralin separated

from the catalyst by distillation under diminished pressure, which requires about 25 minutes. Whilst the autoclave remains under diminished pressure a fresh charge of molten naphthalene is introduced and is hydrogenated in a similar manner, so that a second hydrogenation can be commenced from $1\frac{1}{2}$ –2 hours after the commencement of the first hydrogenation. Several methods are available for the reactivation of the catalyst, but if no satisfactory reactivation process is available, the nickel can be recovered by solution in acid followed by precipitation. The Tetralin obtained is water clear and has a sp.gr. 0.974–0.976 at 20°, setting-point -27° to -30° , b.p. 206° – 208° , flash-point 78° . It is unaffected by exposure to air and light for a long period at the ordinary temperature, but if the hot vapour of anhydrous Tetralin is exposed to air the formation of water is observed, probably as a result of oxidation to dihydronaphthalene (*cf.* Weger, *Ber.* 1903, 36, 309; Ciamician and Silber, *ibid.* 1913, 46, 421; Atti R. Accad. Lincei, 1913, (5), 22, i. 131). It is a valuable crystallising medium, as resins, sulphur, naphthalene, anthracene and many other aromatic hydrocarbons, and other organic substances are extremely soluble in it, particularly when gently warmed. The small proportion of impurities contained in commercial Tetralin can be removed almost completely by fractionation under diminished pressure, but pure tetrahydronaphthalene is best obtained from Tetralin by sulphonation, conversion into the sodium salt, and hydrolysis of the latter, mixed with 72 p.c. sulphuric acid, with superheated steam at 180° – 200° .

β or 1:2:3:4 *Tetrahydronaphthalene* is a colourless oil, volatile with steam, b.p. 206.5° /755 mm., or b.p. 100° – 101° /25 mm., d_4^{20} 0.971 (Schroeter, *l.c.*); molecular heat of combustion at constant pressure $1341.2/20^{\circ}$ (Roth and von Auwers, *l.c.*; *cf.* Leroux, *Compt. rend.* 1910, 151, 384). Tetrahydronaphthalene, prepared by other workers, is a colourless, mobile oil, b.p. 204.5° – 205° /716 mm., sp.gr. 0.978 at 17° (Bamberger and Kitchelt); b.p. 206° /atm., sp.gr. 0.984 at 0° , and 0.966 at 20° , n_D^{20} 1.5402 (Leroux, *Compt. rend.* 1906, 139, 672; *Ann. Chim.* 1910, [8] 21, 458); b.p. 208° – 212° (Ipatiew, *Ber.* 1907, 40, 1287); b.p. 205° , d_4^{20} 0.957, n_D^{20} 1.5370 (von Braun and Deutsch, *Ber.* 1912, 45, 1270); b.p. 204° – 205° (Willstätter and King, *Ber.* 1913, 46, 527), but the product of von Braun and Deutsch, obtained synthetically by the action of aluminium chloride on phenylbutyl chloride, does not appear to be a homogeneous product. A more complete list of physical constants is given by Auwers (*Ber.* 1913, 46, 2988); refractive power (Pellini, *Gazz. chim. ital.* 1901, 31, i. 1); spectrum (Leonard, *Chem. Soc. Trans.* 1910, 97, 1246; Purvis, *ibid.* 1912, 101, 1325); behaviour towards Tesla rays (Kauffmann, *Ber.* 1904, 37, 2945). The following are some of the more recently determined constants: m.p. -35.0° $\pm 0.5^{\circ}$, b.p. 207.3° ; vapour pressure formula

$$\log p = -2681.3/T + 1.75 \log T - 0.003214 T + 5.31446;$$

heat of vaporisation 79.32 cal./gr.; Trouton

constant 21.8 ; ebullioscopic constant 5773 ; specific heat (15° – 18°) 0.403 ; density

$$d_t 0.9843(1 - 763 \times 10^{-6}t);$$

coefficient of expansion (15° – 25°) 0.00078 ; critical temperature 789° ; surface tension at b.p. 17.46 dynes/cm.; molecular surface energy 512.9 (Herz and Schuftan, *Zeitsch. physikal. Chem.* 1922, 101, 269). When tetrahydronaphthalene is treated with much less than one molecular proportion of aluminium chloride at temperatures up to 100° , the principal products are octahydroanthracene and octahydrophenanthrene, whilst a more prolonged reaction produces hydrocarbons of higher molecular weight (Tetralin, G.m.b.H., D. R. P. 333158, 1919), a reaction which was confirmed by Boedtker and Rambech (*Bull. Soc. chim.* 1924, [iv.] 35, 631) and shown to be reversible.

Tetrahydronaphthalene derivatives.—The constitution of tetrahydronaphthalene was determined by Bamberger and Kitchelt (*Ber.* 1890, 23, 1564) by oxidation with alkaline permanganate to *o*-carboxy- β -phenylpropionic acid, but the addition of the requisite quantity of finely-divided permanganate to a hot mixture of tetrahydronaphthalene and water results in the almost quantitative formation of phthalonic acid (von Braun, etc., *Ber.* 1923, 56, 2332).

The *sulphonation* of tetrahydronaphthalene has been studied by Bamberger and Kitchelt (*Ber.* 1890, 23, 1563); Boes (*Ber. Deut. pharm. Ges.* 1902, 12, 222); Friedel and Crafts (*Bull. Soc. chim.* 1884, 42, 66); by Schroeter and Schrauth (D. R. P. 299604, 1916), and by Schroeter, Svanoë, Einbeck, Geller and Riebensahn (*Annalen*, 1922, 426, 111).

The tetrahydronaphthalene sulphonic acid obtained by Graebe and Guye (*Ber.* 1872, 5, 677; 1883, 16, 3028) appears to be 1:4:5:8-*tetrahydronaphthalene sulphonic acid*, crystals, readily soluble in water and alcohol; *sodium salt* tables $+H_2O$; *barium salt* tables $+\frac{1}{2}H_2O$ or $2H_2O$.

ar-Tetrahydronaphthalene α -sulphonic acid was first obtained by Morgan, Micklethwait and Winfield (*Chem. Soc. Trans.* 1904, 85, 736) from *ar-tetrahydro- α -naphthylamine 4-sulphonic acid*, and is formed to the extent of 4–7 p.c. together with the β -isomeride by the sulphonation of tetrahydronaphthalene with concentrated sulphuric acid (Schroeter, &c., *l.c.*). When tetrahydronaphthalene is sulphonated with chlorosulphonic acid below -5° to -10° , a mixture of approximately equal parts of *ar-tetrahydronaphthalene α - and β -sulphonyl chlorides* is obtained, which, after hydrolysis with steam, may be separated by crystallisation from chloroform in which the α -sulphonic acid is less soluble, or by precipitating the lead salt of the α -sulphonic acid from an aqueous solution. *ar-Tetrahydronaphthalene α -sulphonic acid* forms colourless needles $+H_2O$ from chloroform, m.p. 105° – 110° , or $+2H_2O$ from water or mineral acids; *sodium salt*, leaflets $+2H_2O$; *ammonium salt*, readily soluble in water, but crystallises on addition of ammonium chloride; *barium salt* $+3H_2O$; *lead salt*, glistening leaflets $+3H_2O$.

ar-Tetrahydronaphthalene β -sulphonic acid separates from the sulphuric acid sulphonation mixture in crystals $+2H_2O$, m.p. 75° ; *sodium salt*, glistening leaflets $+H_2O$ from water; *am-*

monium salt, silky glistening leaflets; barium salt, glistening leaflets; lead salt, small leaflets + H_2O .

ar-Tetrahydronaphthalene α -sulphonyl chloride, m.p. 70° – 72° ; *sulphonamide*, colourless leaflets, or prisms, m.p. 139° – 140° ; *sulphonanilide*, m.p. 148° – 149° . *ar-Tetrahydronaphthalene β -sulphonyl chloride*, colourless tables, m.p. 58° , b.p. 197° – $200^\circ/18$ mm.; *sulphonamide*, m.p. 135° – 137° ; *sulphonanilide*, m.p. 155° – 156° .

ar-Tetrahydronaphthalene α -sulphonamide is oxidised readily by permanganate to 2-sulphonamino-4-carboxyphenylglyoxylic acid, which is converted by further oxidation into 3-sulphonaminophthalic acid, and *ar-tetrahydronaphthalene β -sulphonamide* gives a mixture of the possible substituted phthalonic acids, converted by further oxidation into 4-sulphonaminophthalic acid (von Braun, etc., Ber. 1923, 56, 2332).

The mixture of α - and β -sulphonyl chlorides, obtained by the action of chlorosulphonic acid on tetrahydronaphthalene, when treated with zinc-dust yields the corresponding *sulphinic acids* (the α -isomeride, colourless needles, decomposing at 103° – 105° , was first prepared by Morgan, Micklethwait and Winfield, *l.c.*) which are converted by zinc and hydrochloric acid into a mixture of *ar-tetrahydronaphthalene- α - and β -thiols*, colourless oil, b.p. 134° – $147^\circ/15$ mm. (the α -thiol, oil, b.p. 141° – $143^\circ/11$ mm., is transformed by methyl sulphate or methyl iodide into *ar-tetrahydronaphthalene- α -methylthiol*, oil, b.p. 158° – $160^\circ/12$ mm.; the β -thiol, colourless oil, b.p. 153° – $155^\circ/26$ mm.; crystalline *mercury salt*; *benzoyl-derivative*, m.p. 98° ; *disulphide*, m.p. 66° ; *ar-tetrahydronaphthalene- β -methylthiol*, colourless oil, b.p. 158° – $159^\circ/10$ mm.). *ar-Tetrahydronaphthalene- α -methylthiol* is converted by oxidation with permanganate in alkaline solution into 2-methylsulphonyl-6-carboxyphenylglyoxylic acid, and this on oxidation in acid solution gives 3-methylsulphonylphthalic acid. The oxidation of *ar-tetrahydronaphthalene- β -methylthiol* with permanganate in alkaline solution, however, gives a mixture of ketonic acids which could scarcely be caused to crystallise, and these on oxidation in acid solution give 4-methylsulphonylphthalic acid (von Braun, etc., *l.c.*). When the mixture of *ar-tetrahydronaphthalene- α - and β -thiols*, in sodium hydroxide solution, is treated with monochloroacetic acid, followed by the addition of ammonium chloride, the ammonium salt of *ar-tetrahydronaphthyl- β -thiolacetic acid* separates in glistening leaflets; *ar-tetrahydronaphthyl- β -thiolacetic acid*, colourless needles, m.p. 78° – 80° . Acidification of the mother liquors yields *ar-tetrahydronaphthyl- α -thiolacetic acid*, colourless glistening leaflets, m.p. 133° – 135° . The latter compound is not converted into a thioindigo derivative as readily as the β -isomeride. *ar-Tetrahydronaphthyl- β -thiolacetic acid* dissolves in fuming sulphuric acid, containing 30 p.c. anhydride, with a yellowish-green colour; when the solution is diluted, boiled and rendered alkaline with sodium hydroxide the sodium salt of *bis-ar-tetrahydrothionaphthene disulphonic acid*, steel blue needles with a copper lustre, is obtained. It dyes wool reddish-violet from an acid bath, and wool or cotton reddish-violet from the vat (Schroeter and Schrauth, D. R. P. 299604, 1916; Tetralin, G.m.b.H.,

D. R. P. 336615, 1919; Eng. Pat. 148419, 1920; Schroeter, &c., *l.c.*).

Halogen derivatives of tetrahydronaphthalene.—Leroux (Compt. rend. 1904, 139, 672; Ann. Chim. 1910, [8] 21, 458) by direct chlorination of tetrahydronaphthalene at low temperatures in diffused light obtained *chlorotetrahydronaphthalene*, oil, b.p. 121° – $124^\circ/15$ mm., or $230^\circ/\text{atm.}$ with evolution of hydrogen chloride, whereas von Braun and Kirschbaum (Ber. 1921, 54, 597) by chlorination, at 100° obtained *ac-1:2-dichlorotetrahydronaphthalene*, b.p. 155° – $160^\circ/20$ mm. *ar- α -Chlorotetrahydronaphthalene*, colourless refractive liquid, b.p. $250^\circ/748$ mm., or b.p. 115° – $116^\circ/12$ mm., cannot be prepared by the action of sodium and amyl alcohol on α -chloronaphthalene, but was obtained by Green and Rowe (Chem. Soc. Trans. 1918, 113, 970) from *ar-tetrahydro- α -naphthylamine* by the diazo-reaction; dinitration yields *ar- α -chloro-2:4-dinitrotetrahydronaphthalene*, colourless plates or needles, m.p. 68° . *ar- α -Chlorotetrahydronaphthalene* is oxidised by alkaline permanganate to a mixture of 3-chlorophthalic acid and 3-chloro-2-carboxyphenylglyoxylic acid, and the mixture of *ar- α - and β -chlorotetrahydronaphthalenes*, b.p. 117° – $130^\circ/17$ mm., obtained by chlorinating tetrahydronaphthalene at 10° in presence of iodine, gives a mixture of 3- and 4-chlorophthalic acids. The exhaustive chlorination of tetrahydronaphthalene in diffused daylight yields *ar-1:2:3:4-tetrachlorotetrahydronaphthalene*, m.p. 172° , b.p. $180^\circ/26$ mm.; *dibromide*, m.p. 142° (von Braun, etc., Ber. 1923, 56, 2332). Leroux (*l.c.*) refers to the direct bromination of tetrahydronaphthalene at low temperatures and obtained a *bromotetrahydronaphthalene*, b.p. 145° – $147^\circ/21$ mm., or $250^\circ/\text{atm.}$ with decomposition, together with the *bromohydrin of a tetrahydronaphthol*, prisms, m.p. 112° , which he considered to be identical with the bromohydrin obtained by Bamberger and Lodter (Annalen, 1895, 288, 74). von Braun and Kirschbaum (*l.c.*), on the other hand, found that tetrahydronaphthalene, which scarcely reacts with bromine in the dark in the absence of a catalyst, is brominated readily in the benzene nucleus in presence of iodine. At higher temperatures, or under the influence of light, however, the hydrogenated ring is attacked, and the only product which could be isolated was *ac-1:2-dibromotetrahydronaphthalene*, m.p. 70° , b.p. 165° – $173^\circ/12$ mm. *ar- α -Bromotetrahydronaphthalene*, b.p. 254° – $256^\circ/758$ mm., was prepared by Smith (Chem. Soc. Trans. 1904, 85, 728) from *ar-tetrahydro- α -naphthylamine*, *ar-1-bromotetrahydro- β -naphthylamine*, and *ar-4-bromotetrahydro- β -naphthylamine* by the diazo-reaction; dinitration yields *ar-1-bromodinitrotetrahydronaphthalene*, pale yellow plates or nodules, m.p. 91° . *ar-2-Bromotetrahydronaphthalene*, obtained from *ar-tetrahydro- β -naphthylamine* by the diazo-reaction, on dinitration yields *ar-2-bromodinitrotetrahydronaphthalene*, pale yellow needles, m.p. 105° – 106° (Morgan, Micklethwait and Winfield, Chem. Soc. Trans., 1904, 85, 736).

ar- α -Bromotetrahydronaphthalene is oxidised by permanganate to a mixture of 3-bromophthalic acid, 2-bromo-6-carboxyphenylglyoxylic acid, and 3-bromo-2-carboxyphenylglyoxylic acid, and successive oxidation with permanganate

in alkaline and acid solution of the mixture of α - and β -bromotetrahydronaphthalenes yields a mixture of 3- and 4-bromophthalic acids (von Braun, etc., *l.c.*).

Nitro-derivatives of tetrahydronaphthalene.—The earlier attempts to prepare nitro-derivatives of tetrahydronaphthalene failed owing to oxidation and resinification taking place, but a number of nitro-derivatives can be obtained in good yield when the nitration is effected under suitable conditions as described by Schroeter, Kindermann, Dietrich, Beyschlag, Fluschhauer, Riebensahn and Oesterlin (Annalen, 1922, 426, 39) and Tetralin, G.m.b.H. (D. R. PP. 299014, 326486, 1916; Eng. Pat. 148923, 1920).

Mononitration is effected either by the use of nitric acid, sp.gr. 1.35, and sulphuric acid, sp.gr. 1.84, at 0°, followed by extraction of the product with carbon tetrachloride, or the use of the latter is avoided by nitrating with a mixture of nitric acid, sp.gr. 1.4, potassium nitrate, and concentrated sulphuric acid, with efficient cooling and agitation; oxidation products are removed by extraction with dilute sodium hydroxide. The residue obtained is a mixture of equal parts of α - and β -nitrotetrahydronaphthalenes, pale yellow oil, b.p. 121°–128°/0.17 mm., sp.gr. 1.184 at 20°. Separation is effected by fractional distillation *in vacuô*, followed by freezing the fractions, or by partial catalytic reduction, when the β -isomeride is converted into the corresponding amine, whilst the α -isomeride remains unaffected.

ar- α -Nitrotetrahydronaphthalene crystallises from methyl alcohol, m.p. 34°, b.p. 157°/13 mm., sp.gr. 1.1757 at 40°; *ar- β -nitrotetrahydronaphthalene*, colourless needles, m.p. 31.4°, b.p. 169°/13 mm., sp.gr. 1.1762 at 40°.

The oxidation of *ar- α -nitrotetrahydronaphthalene* with permanganate yields 2-nitro-6-carboxyphenylglyoxylic acid with a small quantity of 3-nitro-2-carboxyphenylglyoxylic acid and traces of 3-nitrophthalic acid, whereas *ar- β -nitrotetrahydronaphthalene* is converted successively into a mixture of nitrophthalonic acids and 4-nitrophthalic acid. The mixture of α - and β -nitrotetrahydronaphthalenes, obtained by the mononitration of tetrahydronaphthalene, is transformed by successive oxidation with permanganate in alkaline and acid solution into a mixture of 3- and 4-nitrophthalic acids (von Braun, etc., Ber. 1923, 56, 2332).

When *ar- β -nitrotetrahydronaphthalene* is dibrominated, and the thick oily product is distilled *in vacuô*, hydrogen bromide is eliminated at 150° with formation of β -nitronaphthalene, m.p. 76°, b.p. 190°–200°/20 mm. (Tetralin, G.m.b.H., D. R. P. 332593, 1919; von Braun, Hahn and Seemann, Ber. 1922, 55, 1687). When the mixture of α - and β -nitrotetrahydronaphthalenes obtained by the mononitration of tetrahydronaphthalene is sulphonated with fuming sulphuric acid, containing 10 p.c. anhydride, a mixture of *ar-1-nitrotetrahydronaphthalene 3-sulphonic acid* and *ar-2-nitrotetrahydronaphthalene 4-sulphonic acid* is obtained, the former being also obtained by the action of fuming sulphuric acid, containing 10 p.c. anhydride, on *ar- α -nitrotetrahydronaphthalene*. *ar-1-Nitrotetrahydronaphthalene 3-sulphonic acid* crystallises from water and is characterised by a crystalline

amide, m.p. 189°. *ar-2-Nitrotetrahydronaphthalene 4-sulphonic acid* forms a *sodium salt*, needles, soluble in 10 parts of hot water, and in 50 parts of 10 p.c. brine, which is much more soluble than that of the isomeric 1-nitro-3-sulphonic acid; its *amide* crystallises from dilute alcohol, m.p. 211°–212° (Schroeter, &c., *l.c.*).

Dinitration of tetrahydronaphthalene with two molecular proportions of 86 p.c. nitric acid and four molecular proportions of 96 p.c. sulphuric acid, or monohydrate, is commenced at 0° and regulated so that the temperature does not exceed 35°–40° when nitration is complete. A mixture of dinitro-derivatives is obtained in which *ar-1:3-* and *ar-1:2-dinitrotetrahydronaphthalenes* predominate. When the washed and dried product is crystallised from glacial acetic acid, a 60 p.c. yield of a mixture is obtained, which, after repeated crystallisation from a mixture of alcohol and glacial acetic acid, yields a *eutectic mixture* of *ar-1:3-* and *ar-1:2-dinitrotetrahydronaphthalenes*, needles, m.p. 72°–73°. This mixture may be separated into its constituents by crystallisation from sulphuric acid. *ar-1:2-Dinitrotetrahydronaphthalene* forms faintly yellow hexagonal plates, m.p. 102°–103°; *ar-1:3-dinitrotetrahydronaphthalene* forms short stout prisms, m.p. 95°, more soluble in sulphuric acid than the isomeride. The latter compound decomposes when heated, and forms an explosive mixture with potassium chlorate, ammonium nitrate, &c.

Trinitration of tetrahydronaphthalene.—*ar-1:3-Dinitrotetrahydronaphthalene* cannot be nitrated further, whereas the 1:2-isomeride can be converted into a trinitro-derivative. When the eutectic mixture of *ar-1:2-* and *1:3-dinitrotetrahydronaphthalenes* is nitrated, a *eutectic mixture* of *ar-1:3-dinitro-* and *ar-1:2:4-trinitrotetrahydronaphthalenes*, m.p. 82°–83°, is obtained, but when *ar-1:2-dinitrotetrahydronaphthalene* is nitrated with 83 p.c. nitric acid and fuming sulphuric acid, containing 15 p.c. anhydride, at 40°, *ar-1:2:4-trinitrotetrahydronaphthalene*, which crystallises from alcohol and acetic acid, and melts at 94.5°–95°, is obtained (Schroeter, &c., *l.c.*).

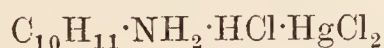
Amino-derivatives of tetrahydronaphthalene.—The reduction of *ar- α -nitrotetrahydronaphthalene* in benzene-alcoholic solution with zinc-dust and hydrochloric acid yields *ar-1:1'-hydrazotetrahydronaphthalene*, long colourless slender needles, m.p. 181°–183°, which is oxidised by permanganate to *ar-1:1'-azotetrahydronaphthalene*, glistening garnet-red needles, m.p. 190°–191°. The latter compound is formed together with *ar-1:1'-azoxytetrahydronaphthalene*, straw-yellow stout needles, m.p. 184°, by a less energetic reduction of *ar- α -nitrotetrahydronaphthalene* with zinc-dust and sodium hydroxide. The application of the benzidine conversion to hydrazotetrahydronaphthalene results in the formation of *ar-4:4'-diamino-1:1'-bis-tetrahydronaphthyl*, m.p. 153°–154°, which forms a sparingly soluble *dihydrochloride* and a more readily soluble *sulphate*, together with a *diamine*, probably *ar-1:1'-diamino-2:2'-bis-tetrahydronaphthyl*, slender white needles, m.p. 216°, which forms a readily soluble *dihydrochloride*, and is converted readily into the corresponding *imide*, a carbazole-like substance, forming a brown crystalline *picrate*.

When *ar*-4:4'-diamino-1:1'-bis-tetrahydronaphthyl is tetrazotised, reduction yields *ar*-4:4'-dihydrazino-1:1'-bis-tetrahydronaphthyl, whilst heating with ethyl alcohol results in the formation of *ar*-4:4'-diethoxy-1:1'-bis-tetrahydronaphthyl, colourless needles, m.p. 173° (Schroeter, &c., *l.c.*; Tetralin, G.m.b.H., D. R. P. 333157, 1916; Eng. Pat. 170867, 1920).

ar-Tetrahydro- α -naphthylamine is obtained by the reduction of α -naphthylamine with sodium and amyl alcohol (Bamberger, Ber. 1887, 20, 2916; Bamberger and Althausse, *ibid.* 1888, 21, 1786); by reduction with sodium and an alcohol in presence of an inert solvent, provided the conditions permit of the isomerisation of the intermediate *ar*-5:8-dihydro- α -naphthylamine (F. Bayer & Co., D. R. PP. 305347, 306724 of 1915; cf. Rowe, J. Soc. Dyers, 1919, 35, 130; J. Soc. Chem. Ind. 1920, 39, 241 T), or the alcohol may be replaced by water (Chem. Fabr. Griesheim-Elektron, D. R. P. 370974); by the reduction of *ar*- α -nitrotetrahydronaphthalene with hydrogen under a pressure of 10–20 atmospheres at 120° in presence of a catalyst; or by the reduction of the mononitration mixture of *ar*- α - and β -nitrotetrahydronaphthalene in a similar manner, the amines being separated by taking advantage of the difference in solubility of their hydrochlorides in water, or of their methane disulphonates in 96 p.c. alcohol, or of the difference in the ease with which the bases are acetylated (Schroeter, &c., *l.c.*; Tetralin, G.m.b.H., D. R. P. 333157, 1916); or by passing α -naphthylamine with pure hydrogen over reduced nickel at 135°–145°, when 90 p.c. of the α -naphthylamine is converted into *ar*-tetrahydro- α -naphthylamine, the remainder being tetrahydronaphthalene formed from acetetrahydro- α -naphthylamine (Komatsu and Nodzu, Mem. Coll. Sci. Kyoto, 1923, 6, 177); and also by the hydrolysis of acetone-*ar*-tetrahydro- α -naphthyl with boiling (20 p.c.) hydrochloric acid (Knoevenagel, Ber. 1922, 55, 2309).

ar-Tetrahydro- α -naphthylamine is a colourless, non-fluorescent oil, which darkens on exposure to air, with an odour slightly resembling that of dimethylaniline, b.p. 275°/712 mm. (Bamberger and Althausse), or 146°/12 mm. (Schroeter), or b.p. 234°/250 mm. (Perkin, Chem. Soc. Trans. 1896, 69, 1004); molecular rotation 20.058 (Perkin, *l.c.*); *hydrochloride*, tetragonal plates; *sulphate* + $\frac{1}{2}$ H₂O, flat needles or silvery plates; *oxalate*, white needles; *nitrate*, glistening plates; *ferrocyanide*, glittering needles; *picrate*, yellow prisms (Bamberger and Althausse, *l.c.*).

ar-Tetrahydro- α -naphthylamine combines with mercuric chloride to form



m.p. 179°–180°; 2(C₁₀H₁₁·NH₂·HCl)·HgCl₂, doubly refracting plates, m.p. 217.5°–219°; C₁₀H₁₁·NH₂·HCl·2HgCl₂, colourless prismatic needles, m.p. 192.5°–193.5° (Grohmann and Brouwer, Annalen, 1909, 365, 50). On oxidation with alkaline permanganate the hydro-base yields a mixture of adipic and oxalic acids, whilst conversion into α -naphthylamine is readily effected by means of platinic chloride, and oxalic acid seems to produce the same result (Bamberger and Althausse, Ber. 1888, 21, 1892). When, however, the oxidation is carried out with sodium bichromate and sulphuric acid, *ar*-

tetrahydro- α -naphthaquinone, m.p. 55.5°, closely resembling benzoquinone in all its properties, is obtained. This same oxidation product is obtained when the oxidation is carried out electrolytically, using platinum, lead peroxide and graphite as anode material, a concentration of sulphuric acid between 10 p.c. and 30 p.c., a temperature of 18°–23°, and a current density of about 1 amp./100 sq. cm. (Ono, Mem. Coll. Sci. Kyoto, 1922, 5, 345). *ar*-Tetrahydro- α -naphthaquinone, on treatment with phenylhydrazine, or when digested for 48 hours with sulphurous acid, yields *ar*-tetrahydro- α -naphthaquinol, crystallising in aggregates of slender colourless prisms which sublime without decomposition forming needles, m.p. 172°–172.5°.

ar-Tetrahydro- α -naphthaquinol is oxidised by potassium dichromate in the cold to the *quinhydrone*, further oxidation resulting in the regeneration of *ar*-tetrahydro- α -naphthaquinone (Bamberger and Lengfeld, Ber. 1890, 23, 1124).

ar-Tetrahydroaceto- α -naphthalide forms glistening needles, m.p. 158°; *ar*-tetrahydro- α -naphthylphenyl-carbamide, needles, m.p. 193°; *ar*-tetrahydro- α -naphthylphenyl-thiocarbamide, m.p. 153°; *bis-ar*-tetrahydro- α -naphthyl-thiocarbamide, lustrous needles, m.p. 170° (Bamberger and Althausse, Ber. 1888, 21, 1786). The latter compound on treatment with α -naphthylamine and lead oxide in alcoholic solution yields *α -naphthyl-ar-tetrahydro- α -naphthyl-guanidine*, microscopic prisms, m.p. 177°–179° (Schall, J. pr. Chem. 1901, [ii] 64, 261). *Benzylidene-ar-tetrahydro- α -naphthylamine* forms rhombic prisms, m.p. 61.5° (Rowe and Levin, Chem. Soc. Trans. 1920, 117, 1579).

ar-Tetrahydro- α -naphthylamine reacts readily with acetyl-acetone forming the *compound*, C₁₀H₁₁N:C(CH₃)·CH₂·COCH₃, viscous liquid, b.p. 208°/15 mm., which is converted by concentrated sulphuric acid into *ar*-2:4-dimethyltetrahydro- α -naphthaquinoline, m.p. 49°, b.p. 196°–200°/15 mm. (von Braun, Gmelin, Petzold and Müncker, Ber. 1924, 57, 390).

ar-Tetrahydro- α -naphthylamine yields a *methane disulphonate*, colourless leaflets, approximately six times as soluble in alcohol as the β -isomeride; with phthalic anhydride it forms *ar*-tetrahydro- α -phthalamide acid, colourless needles, m.p. 182°–184° (decomp.), which when heated to about 200° is converted into the corresponding *phthalimide*, long colourless needles, m.p. 148°–150°. *ar*-Tetrahydroaceto- α -naphthalide sodium, white powder, is obtained by the action of sodium on a solution of *ar*-tetrahydroaceto- α -naphthalide in toluene; when boiled with dimethyl sulphate and the product distilled *in vacuo*, the acetyl derivative of *ar*-tetrahydro-methyl- α -naphthylamine, colourless needles, m.p. 70°–72°, b.p. 182°–185°/11 mm., is obtained (Schroeter, &c., *l.c.*).

ar-Tetrahydronaphthalene- α -diazonium chloride forms glistening needles which explode on heating; *ar*-tetrahydro- α -naphthonitrile, colourless viscid oil, b.p. 277°–279°/721 mm., or pale yellow crystals, m.p. 48°, b.p. 153°/15 mm. (von Braun, etc., Ber. 1922, 55, 1700); *ar*-tetrahydro- α -naphthothiamide, dark yellow oil; *ar*-tetrahydro- α -naphthamide, flat needles, m.p. 182°; *ar*-tetrahydro- α -naphthylhydrazine, white prisms, forms a *hydrochloride*, silvery scales (Bamberger and Bordt, Ber. 1889, 22, 625).

ar-Tetrahydro- α -naphthylpiperidine, obtained by the reduction of *α -naphthylpiperidine* with sodium and amyl alcohol, forms a pale yellow oil, b.p. 218°/63 mm.; the *hydrochloride* crystallises with difficulty; *mercury chloride*, amorphous powder; *ferrocyanide*, white crystals; *platinochloride*, small lustrous crystals, m.p. 190°–192°; *aurichloride*, golden-yellow crystals (Abel, Ber. 1895, 28, 3106).

The main products of the reduction of *α -naphthonitrile* with sodium and absolute alcohol are dihydronaphthalene and *ac-tetrahydro- α -naphthylmethylaniline*, colourless, strongly refractive, viscid oil of peculiar ammoniacal odour, b.p. 269°–270°/722 mm., with a remarkable affinity for carbon dioxide; *hydrochloride*, needles, m.p. 230°; *platinochloride*, yellow crystalline powder; *picrate*, glistening yellow needles, m.p. 169°–170° (Bamberger and Lodter, Ber. 1887, 20, 1703); *acetyl derivative*, nacreous plates, m.p. about 88.5°; *benzoyl derivative*, m.p. 125°; *phenyl-carbamide* colourless needles, m.p. 126.5° (Bamberger and Lodter, Ber. 1887, 20, 1702, 1703; Bamberger and Helwig, Ber. 1889, 22, 1912; von Braun, etc., Ber. 1922, 55, 1700, 3664).

When the acetyl, formyl, propionyl or benzoyl derivative of *ar-tetrahydro- α -naphthylamine* is brominated in glacial acetic acid or chloroform solution, or treated with hypobromous acid, intermediate *perbromides* are obtained, which on keeping or warming are converted into 4-bromo-substitution products; *ar-4-bromotetrahydroaceto- α -naphthalide*, needles, m.p. 180°–181° (Bamberger and Althausse, l.c.); *formyl-*ar-4-bromotetrahydro- α -naphthylamine**, colourless plates, m.p. 164.5°; *propionyl-*ar-4-bromotetrahydro- α -naphthylamine**, colourless needles, m.p. 185°–186°; *benzoyl-*ar-4-bromotetrahydro- α -naphthylamine**, colourless needles, m.p. 202°–203°; all of which on hydrolysis yield *ar-4-bromotetrahydro- α -naphthylamine*, colourless needles, m.p. 42° (Morgan, Micklethwait and Winfield, Chem. Soc. Trans. 1904, 85, 736).

The sulphonation of *ar-tetrahydro- α -naphthylamine* with concentrated sulphuric acid or with fuming sulphuric acid, containing 10 p.c. anhydride, yields *ar-tetrahydro- α -naphthylamine 4-sulphonic acid*, colourless acicular prisms + H₂O, *barium salt* + 3H₂O, *sodium salt*; *ar-tetrahydro- α -naphthylamine 3-sulphonic acid*, faintly coloured leaflets, is formed by the reduction of the corresponding nitro-compound. When *ar-tetrahydro- α -naphthylamine 3-sulphonic acid*, or its condensation product with *p-toluene sulphonyl chloride*, is submitted to alkaline fusion *ar-tetrahydro- α -naphthylamine* is obtained (Schroeter, etc., Annalen, 1921, 426, 17).

The main product of the nitration of *ar-tetrahydroaceto- α -naphthalide* with mixed acid is *ar-4-nitrotetrahydroaceto- α -naphthalide*, colourless slender needles, m.p. 178° (Green and Rowe, Chem. Soc. Trans. 1918, 113, 959), or 175°–176° (Schroeter, &c.), and the latter authors also isolated *ar-2-nitrotetrahydroaceto- α -naphthalide*, colourless needles, m.p. 184°–185°, together with a small proportion of *ar-3-nitrotetrahydroaceto- α -naphthalide*, m.p. 193°. The hydrolysis of these acetyl derivatives yields respectively *ar-4-nitro- α -naphthylamine*, pale yellow needles, m.p. 116° (Green and Rowe), or 114°–116° (Schroeter, &c.), *ar-2-nitrotetrahydro-*

α -naphthylamine, long orange-coloured needles, m.p. 87°–88°, and *ar-3-nitrotetrahydro- α -naphthylamine*, yellow leaflets, m.p. 78°, this being identical with the product obtained by the partial reduction of *ar-1:3-dinitrotetrahydro-naphthalene*.

The dinitration of *ar-tetrahydroaceto- α -naphthalide* yields *ar-2:4-dinitrotetrahydroaceto- α -naphthalide*, colourless needles, m.p. 202° (Green and Rowe), or 204° (Schroeter, &c.), whilst *ar-2:4-dinitrotetrahydro- α -naphthylamine*, yellow needles, m.p. 181° (Green and Rowe), or 184° (Schroeter, &c.), is obtained from it by hydrolysis with sulphuric acid (Schroeter, &c., l.c.; Green and Rowe, Chem. Soc. Trans. 1918, 113, 955).

The sole product of the action of sodium and amyl alcohol on 1:4-naphthylenediamine is the *ar-tetrahydro-derivative* (Bamberger and Schieffelin, Ber. 1889, 22, 1382), which is also formed by the reduction of *ar-tetrahydro- α -naphthylamine-4-azobenzene-4'-sulphonic acid* (Morgan, Micklethwait and Winfield), or by the reduction of *ar-4-nitrotetrahydro- α -naphthylamine* (Green and Rowe; Schroeter, &c.). *ar-Tetrahydro-1:4-naphthylenediamine* forms colourless needles, m.p. 83°–85°, b.p. 203°/18 mm.; *hydrochloride*, colourless glistening leaflets; *monoacetyl-*ar-tetrahydro-1:4-naphthylenediamine**, colourless rhombic plates or needles, m.p. 156° (Green and Rowe), or 154°–156° (Schroeter, &c.), is obtained by the reduction of *ar-4-nitrotetrahydroaceto- α -naphthalide*; *1:4-diacetyl-*ar-tetrahydro-1:4-naphthylenediamine**, colourless needles, m.p. 291°–292° (Schroeter, &c., l.c.), or 285° (Bamberger and Schieffelin, l.c.); *ar-tetrahydro-1:4-naphthylene-dichlorodiimide* forms long silky yellowish-white needles, m.p. 68° (Bamberger, Annalen, 1890, 257, 1). The product of the action of sodium and amyl alcohol on 1:5-naphthylenediamine is *tetrahydro-1:5-naphthylenediamine*, needles or prisms, coloured by exposure to air, m.p. 77°, b.p. 264°/60 mm., slightly volatile with steam. This compound is of particular interest as it combines both alicyclic and aromatic properties, thus only the amino-group in the non-hydrogenated ring can be diazotised, whilst the presence of an amino-group in the hydrogenated ring renders it such a strong base that it readily forms a *carbonate*, lustrous crystalline powder; *dihydrochloride*, strongly refractive rhombic prisms; *sulphate*, lustrous triclinic prisms + 2H₂O; *platinochloride*, orange-coloured crystals (Bamberger and Hoskyns-Abraham, Ber. 1889, 22, 943); *1:5-diacetyl-ac-*ar-tetrahydro-1:5-naphthylenediamine**, slender silky prisms, m.p. 262°. When the diazonium chloride of the hydro-base is reduced with stannous chloride, *ac-tetrahydro-1-amino-5-naphthylhydrazine*, brown oil, is obtained; *hydrochloride*, prisms or lozenge-shaped plates, m.p. 265°. *ac-*ar-1:5-Tetrahydronaphthylenediamine-ac-tetrahydroaminonaphthyl thiocarbamate**, lustrous crystalline powder, m.p. 145°, is obtained by the action of carbon disulphide on a cold ethereal solution of the tetrahydro-1:5-diamine, but when the condensation product is boiled with alcohol, hydrogen sulphide is evolved with the formation of *diamino-bis-tetrahydronaphthyl thiocarbamide*, which sinters at 120° and melts at 155°. When an alcoholic solution of the thiocarba-

mate is boiled with lead oxide *diamino-bis-tetrahydronaphthyl-carbamide*, white crystalline powder, softening at 70°, decomposing at 135°, is obtained, whilst when the *ac-ar-tetrahydro-1:5-diamine* is boiled with excess of carbon disulphide, *bis-tetrahydronaphthyl-bis-thio-carbamide*, white crystalline powder, m.p. 175°, is formed (Bamberger and Bammann, Ber. 1889, 22, 951).

The reduction of ethyl- α -naphthylamine with sodium and amyl alcohol results in the sole formation of *ar-tetrahydroethyl- α -naphthylamine*, colourless mobile oil, b.p. 286°–287°/717 mm., with an odour faintly resembling that of dimethylaniline; *hydrochloride*, needles which effloresce at 80°–90°, m.p. 118°; *platinochloride*, golden-yellow plates. When a solution of *ar-tetrahydroethyl- α -naphthylamine hydrochloride* is treated with sodium nitrite the *nitrosoamine* separates as an oil, but when an alcoholic hydrochloric acid solution of the latter compound is kept for some time *ar-4-nitrosotetrahydroethyl- α -naphthylamine hydrochloride* separates in golden prisms or needles; *ar-4-nitrosotetrahydroethyl- α -naphthylamine*, silky golden needles, m.p. 119°, yields on reduction *ar-4-aminotetrahydroethyl- α -naphthylamine* (Bamberger and Helwig, Ber. 1889, 22, 1311). *ar-Tetrahydrodimethyl- α -naphthylamine*, colourless mobile oil, which turns brown on exposure to air, b.p. 261°–262°/721 mm., or 131°–131.5°/16 mm., is obtained by the action of sodium and amyl alcohol on dimethyl- α -naphthylamine (Bamberger and Helwig, *l.c.*) or by heating *ar-tetrahydro- α -naphthylamine hydrochloride* with methyl alcohol at 170°–180° (Morgan and Richards, J. Soc. Chem. Ind. 1905, 24, 652); *hydrochloride*, a syrup; *platinochloride*, orange-yellow crystals; *methiodide*, glistening prisms, m.p. 164.5°; *ar-4-nitrosotetrahydrodimethyl- α -naphthylamine*, unstable oil.

ar-Tetrahydrodimethyl- α -naphthylamine reacts with methyl iodide more readily than dimethyl-*o*-toluidine, and when warmed with cyanogen bromide yields *ar-tetrahydrocyano-methyl- α -naphthylamine*, b.p. 179°–180°/7 mm., from which on hydrolysis *ar-tetrahydromethyl- α -naphthylamine*, pale yellow oil, b.p. 150°–152°/12 mm., is obtained (*picrate*, m.p. 174°, *thiocarbamide derivative*, colourless plates, m.p. 113°).

ar-Tetrahydrodimethyl- α -naphthylamine on treatment with formaldehyde and hydrochloric acid yields *ar-4-hydroxymethyl-tetrahydrodimethyl- α -naphthylamine*, viscous, yellow oil, b.p. 189°–196°/10 mm.; *picrate*, m.p. 92°–94° (von Braun, Arkuszewski and Köhler, Ber. 1918, 51, 282).

ar-Tetrahydro- α -naphthylmethylamine is obtained together with tetrahydronaphthalene by reduction of *ar-tetrahydro- α -naphthonitrile* with sodium and alcohol, but contrary to the observations of Bamberger and Lodter (Ber. 1887, 20, 1703) it is prepared conveniently by the action of sodium and amyl alcohol on α -naphthylmethylamine (von Braun, Moldaenke, Dirlam and Gruber, Ber. 1922, 55, 1700); treatment of α -naphthonitrile at 190° with hydrogen in presence of a nickel catalyst gives rise to α -naphthylmethylamine and the nucleus is not hydrogenated, but a solution of *ar-tetrahydro- α -naphthonitrile* in five parts of tetrahydronaphthalene is reduced catalytically by hydrogen

to *ar-tetrahydro- α -naphthylmethylamine* in 70 p.c. yield, together with *bis-ar-tetrahydro- α -naphthylmethylamine*, m.p. 93° (*hydrochloride*, m.p. 212°; *nitroso-derivative*, m.p. 90°–91°) (von Braun, Blessing and Zobel, Ber. 1923, 56 1988). *ar-Tetrahydro- α -naphthylmethylamine* is a colourless liquid, b.p. 149°–152°/11 mm.; *hydrochloride*, lustrous needles, m.p. 253°; *picrate*, prisms, m.p. 242°; *acetyl-derivative*, m.p. 125°; *benzoyl-derivative*, m.p. 144°; *phenyl-carbamide*, m.p. 199°; *phenylthiocarbamide*, m.p. 153°.

ar-1-Benzoylaminomethyltetrahydronaphthalene is converted by phosphorus pentachloride into *ar-1-chloromethyltetrahydronaphthalene*, b.p. 144°–145°/13 mm., m.p. 50°–51° (*ar-2-chloromethyltetrahydronaphthalene* has b.p. 141°–142°/12 mm. but does not solidify on cooling). Potassium cyanide in aqueous alcoholic solution converts it into *ar-1-cyanomethyltetrahydronaphthalene*, colourless needles, m.p. 69°–70°, b.p. 168°–169°/10 mm., which, on reduction with sodium and alcohol, yields *ar-1- β -aminomethyltetrahydronaphthalene*, colourless, viscous liquid, b.p. 146°–149°/16 mm., *hydrochloride*, m.p. 245° (decomp.), *picrate*, small leaflets, m.p. 231°, *benzoyl derivative*, m.p. 123° (von Braun, Gruber and Kirschbaum, Ber. 1922, 55, 3664). The condensation of 1-chloro-2:4-dinitrobenzene with *ar-tetrahydro- α -naphthylamine* yields *ar-2:4-dinitrophenyl-tetrahydro- α -naphthylamine*, red leaflets, m.p. 134° (Green and Rowe, Chem. Soc. Trans. 1918, 113, 955).

ac-Tetrahydro- α -naphthylamine, clear viscid oil, b.p. 246.5°/714 mm., is obtained by the action of a 10 p.c. solution of copper sulphate on *ac-tetrahydro-1-amino-5-naphthylhydrazine* (Bamberger and Bammann, Ber. 1889, 22, 951). It is formed to a very limited extent in the reduction of α -naphthylamine with sodium and amyl alcohol (Green and Rowe, *l.c.*), also by the reduction of the oxime of *ac-1-ketotetrahydronaphthalene* with sodium amalgam and dilute acetic acid (Kipping and Hill, Chem. Soc. Trans. 1889, 75, 144), or in 90 p.c. yield by reduction with sodium and alcohol (von Braun, Braunsdorf and Kirschbaum, Ber. 1922, 55, 3648). *ac-Tetrahydro- α -naphthylamine* is a strong base which cannot be diazotised; it forms a *carbonate*, glistening needles; a *nitrite*, long lustrous needles, m.p. 138°–139°, which is unaffected by boiling water; a *hydrochloride*, lustrous needles; a *platinochloride*, orange-coloured prisms, m.p. 190°, the melting point varying greatly with the rate of heating; a *picrate*, glistening needles; an *acetyl derivative*, long prisms or silky needles, m.p. 148°–149° (Bamberger), or 144°–145° (Kipping and Hill). *Diazobenzene-ac-tetrahydro- α -naphthylamine*, obtained by the addition of diazobenzene nitrate to an aqueous suspension of *ac-tetrahydro- α -naphthylamine*, crystallises in lustrous yellow needles, and forms a *picrate*, silky sulphur-coloured needles, which darken at 215° and melt at 229°–230° (decomp.). *5-Hydroxy-ac-tetrahydro- α -naphthylamine* (or *ac-tetrahydro-1:5-aminonaphthol*), a colourless oil of sharp ammoniacal odour, is prepared from *ac-ar-tetrahydro-1:5-naphthylenediamine* by the diazo-reaction; *hydrochloride*, long glassy needles, m.p. 220°; *picrate*, branched lustrous needles; *diacetyl derivative*, lustrous white

needles, m.p. 151° – 151.5° (Bamberger and Bammann, *l.c.*). *ac-Tetrahydro- α -naphthylcarbamide*, needles, m.p. 210.5° , is formed by the action of potassium cyanate on *ac-tetrahydro- α -naphthylamine* (Schroeter and Thomas, *Zeitsch. physiol. Chem.* 1918, 101, 262); *ac-2:4-dinitrophenyltetrahydro- α -naphthylamine*, golden-yellow plates, m.p. 121° (Green and Rowe, *Chem. Soc. Trans.* 1918, 113, 955).

ac-Tetrahydro- α -naphthylamine is converted by *α - ϵ -dibromopentane* in boiling alcoholic solution into *ac-1-piperidinotetrahydronaphthalene*, colourless liquid, b.p. 174° – 176° , which forms an uncrystallisable *hydrochloride*, *hydrobromide*, and *methiodide*, an amorphous *chloroplatinate*, and a *picrate*, dark yellow needles, m.p. 145° – 146° after softening at 140° (von Braun, Braunsdorf and Kirschbaum, *Ber.* 1922, 55, 3648).

ar-Tetrahydro- β -naphthylamine is formed to the extent of 3–4 p.c., together with its alicyclic isomeride, by the reduction of *β -naphthylamine* in amyl alcoholic solution with an increased amount of sodium, viz. 20 grms. of sodium to 15 grms. of the amine (Bamberger and Kitschelt, *Ber.* 1890, 23, 876; cf. Lindner, Djulgerowa and Mayr, *Monatsh.* 1924, 44, 337); by converting *ar-tetrahydro- β -naphthylmethyl ketone* into the oxime, and submitting the latter to the Beckmann reaction, followed by hydrolysis of the resulting acetyl derivative (Scharwin, *Ber.* 1902, 35, 2511); by treatment of the amide of *ar-tetrahydro- β -naphthoic acid* with bromine and alkali (von Braun, Kirschbaum and Schuhmann, *Ber.* 1920, 53, 1161); by the catalytic reduction of *ar- β -nitrotetrahydronaphthalene*; or by the catalytic reduction of the products of the mononitration of *tetrahydronaphthalene*, the amino-derivatives being separated as indicated in the case of *ar-tetrahydro- α -naphthylamine* (Schroeter, &c., *Annalen*, 1921, 426, 17; D. R. P. 333157, 1916). Its constitution was determined by oxidation to adipic acid with alkaline permanganate (Bamberger and Kitschelt, *l.c.*). *ar-Tetrahydro- β -naphthylamine*, lustrous, silvery, flat needles, m.p. 38° , b.p. 275° – 277° /713 mm. (Bamberger and Kitschelt), m.p. 38.5° – 39.5° , b.p. 147° – 148° /13 mm. (Schroeter), resembles aniline in its odour and *ar-tetrahydro- α -naphthylamine* in its properties; the *hydrochloride*, large colourless plates, and *sulphate* are sparingly soluble in cold water and six times less soluble in alcohol than the salts of the *α -isomeride*; *acetyl derivative*, m.p. 107° ; *benzoyl derivative*, colourless needles, m.p. 166° – 167° . With phthalic anhydride it forms a *phthalamic acid*, glistening needles, m.p. 156° – 158.5° , with elimination of the elements of water; the phthalamic acid when heated to 185° is converted into the corresponding *phthalimide*, needles, m.p. 169° – 171° . *ar-Tetrahydroaceto- β -naphthalide sodium*, white powder, obtained by the action of sodium on a solution of *ar-tetrahydroaceto- β -naphthalide* in toluene, when treated with dimethyl sulphate and the product distilled *in vacuô* yields the *acetyl derivative of ar-tetrahydromethyl- β -naphthylamine*, needles, m.p. 67° – 69° , b.p. 178° – 180° /12 mm. (Schroeter, &c., *l.c.*; Scharwin, *l.c.*). *β -Naphthylpiperidine*, on treatment with sodium in alcoholic solution is reduced to *ar-tetrahydro- β -naphthyl-*

piperidine, oil, b.p. 274° – 276° /749 mm., or 190° – 196° /24 mm., a weak base of unpleasant odour, which does not absorb carbon dioxide from the air, and is without physiological action; *hydrochloride*, colourless glistening crystals, m.p. 210° – 211° ; *mercury double salt*, oil; *platinochloride* + $3\text{H}_2\text{O}$, m.p. 156° – 159° ; *aurochloride*, m.p. 135° ; *picrate*, m.p. 166° (Roth, *Ber.* 1896, 29, 1178). *ar-Tetrahydro- β -naphthylcarbamide*, needles, m.p. 134° (decomp.) is formed by the action of potassium cyanate on the tetrahydro-base, a substance, m.p. above 245° , apparently *bis-ar-tetrahydro- β -naphthylcarbamide* being formed at the same time (Schroeter and Thomas, *Zeitsch. physiol. Chem.* 1918, 101, 262). When the products of the mononitration of *tetrahydronaphthalene* (a mixture of *ar- α -* and *β -nitrotetrahydronaphthalenes*) are sulphonated, a mixture of *ar-1-nitrotetrahydronaphthalene 3-sulphonic acid* and *ar-2-nitrotetrahydronaphthalene 4-sulphonic acid* is produced, the sodium salt of the latter being much more soluble than that of the former. *ar-2-Nitrotetrahydronaphthalene 4-sulphonic acid*, on catalytic reduction, yields *ar-tetrahydro- β -naphthylamine 4-sulphonic acid*; *hydrochloride*, soluble in 120 parts of hot water (Schroeter, &c., *l.c.*).

ar-Tetrahydro- β -naphthylamine, when submitted to the Skraup reaction, gives rise to a mixture of 7:8:9:10-*tetrahydro- β -naphthaaquinoline*, colourless, crystalline compound, which becomes pink on exposure to air, m.p. 158° , b.p. 183° – 185° /12 mm. (*hydrochloride*, m.p. 236° , after darkening at 226° ; *picrate*, m.p. 207° ; *methiodide*, m.p. 203°), and 6:7:8:9-*tetrahydronaphthazine*, colourless, crystalline compound, m.p. 71° – 72° , b.p. 187° /11 mm. (*hydrochloride*, pale yellow needles, m.p. 177° ; *picrate*, m.p. 269.5° ; *methiodide*, m.p. 187°). The former base is dehydrogenated at 700° and the latter at 720° , yielding *β -naphthaaquinoline*, m.p. 91° – 92° , and *naphthazine*, colourless crystals, m.p. 114° , b.p. 200° – 205° /14 mm., respectively. Treatment of *naphthazine* with tin in concentrated hydrochloric acid effects hydrogenation in the pyridine ring (von Braun and Gruber, *Ber.* 1922, 55, 1710).

The course of the quinaldine synthesis with *ar-tetrahydro- β -naphthylamine* has been investigated by Lindner, Djulgerowa and Mayr (*Monatsh.* 1924, 44, 336), who found that both the linear and angular compound are produced. 6:7-*Tetramethylenequinaldine*, m.p. 45° ; *hydrochloride*, m.p. 209° – 212° ; *hydrobromide*, m.p. 212° ; *picrate*, m.p. 206° . 5:6-*Tetramethylenequinaldine*, m.p. 57° ; *hydrochloride*, m.p. about 240° ; *hydrobromide*, m.p. 220° ; *picrate*, m.p. 190° .

ar-Tetrahydroaceto- β -naphthalide, when brominated in glacial acetic acid at 50° – 60° with one molecular proportion of bromine, yields a mixture of *ar-1-bromotetrahydroaceto- β -naphthalide*, colourless octahedral crystals, m.p. 125.5° , and *ar-4-bromotetrahydroaceto- β -naphthalide*, colourless needles, m.p. 151° , in the proportion of 7:1; separation is effected by taking advantage of the greater solubility of the latter in acetic acid. On hydrolysis with alcoholic hydrochloric acid they yield respectively, *ar-1-bromotetrahydro- β -naphthylamine*, colourless silky needles, m.p. 52.5° , volatile with steam, *hydrochloride*, long white needles, moderately soluble in hot water with partial dissociation;

and *ar*-4-bromotetrahydro- β -naphthylamine, colourless needles, m.p. 52°, not volatile with steam, *hydrochloride*, long prismatic needles. The production of these compounds is of interest, for, as a result of the introduction of 4 atoms of hydrogen into the non-substituted ring of β -naphthylamine, the hydrogen atom in the α -position adjacent to the amino-group, which so readily undergoes substitution in β -naphthylamine, has to a great extent lost its reactivity in *ar*-tetrahydro- β -naphthylamine, and is comparable with the hydrogen atom in the o -position with respect to the amino-group in a benzenoid amine. Thus, the naphthalenoid character of β -naphthylamine has been lost, for the latter on halogenation even with excess of halogen yields only the 1-substituted derivative (Smith, Chem. Soc. Trans. 1904, 85, 728).

By the regulated addition of a mixture of nitric acid, sp.gr. 1.4, and sulphuric acid, sp.gr. 1.4, to a solution of *ar*-tetrahydroaceto- β -naphthalide in glacial acetic acid solution keeping the temperature below 45°, a mixture of *ar*-3-nitrotetrahydroaceto- β -naphthalide, long yellow needles, m.p. 134°–135.5°, and *ar*-1-nitrotetrahydroaceto- β -naphthalide, colourless needles, m.p. 128°–129°, is formed, which can be separated by crystallisation from alcohol, in which the latter is more readily soluble. The former product is also obtained, but in smaller quantity, by nitrating *ar*-tetrahydroaceto- β -naphthalide in concentrated sulphuric acid solution with mixed acid below 0°, the main product in this case being *ar*-4-nitrotetrahydroaceto- β -naphthalide, long colourless needles, m.p. 194°, which separates from hot alcohol on cooling, whilst the 3-nitro-isomeride mentioned above remains in solution. These acetyl compounds on hydrolysis yield respectively *ar*-3-nitrotetrahydro- β -naphthylamine, long red needles, m.p. 125°–127°; *ar*-1-nitrotetrahydro- β -naphthylamine, red needles, m.p. 96°, identical with the product of the partial reduction with stannous chloride of *ar*-1:2-dinitrotetrahydronaphthalene, or of its eutectic mixture with *ar*-1:3-dinitrotetrahydronaphthalene; *ar*-4-nitrotetrahydro- β -naphthylamine, yellow crystalline powder, m.p. 55°, identical with the by-product of the partial reduction of *ar*-1:3-dinitrotetrahydronaphthalene with stannous chloride, and with the main product of the partial reduction of *ar*-1:3-dinitrotetrahydronaphthalene in tetrahydronaphthalene solution at 180° with hydrogen under pressure in the presence of a catalyst; *sulphate*, large colourless plates. The yield of the nitroamines, produced as indicated, is dependent upon the nature of the reducing agent.

ar-1:3-Dinitrotetrahydroaceto- β -naphthalide, colourless needles, m.p. 189°–191°, is obtained by the further nitration of *ar*-1-nitrotetrahydroaceto- β -naphthalide, or of *ar*-3-nitrotetrahydroaceto- β -naphthalide in sulphuric acid solution with mixed acid and good cooling; it is also found as a by-product in the mother-liquors of the nitration products obtained by the direct dinitration of *ar*-tetrahydroaceto- β -naphthalide. When it is formed from the 3-nitro-compound, an *isomeride*, turning brown at 175° and decomposing at about 215°, is also formed. On hydrolysis, the 1:3-dinitroacetyl derivative yields *ar* 1:3-dinitrotetrahydro- β -naphthylamine, glistening yellow needles, m.p. 166°–168°.

ar-3:4-Dinitrotetrahydroaceto- β -naphthalide, needles, m.p. 175°–177°, is the main product obtained by the dinitration of *ar*-tetrahydroaceto- β -naphthalide in sulphuric acid solution, and by the further nitration of *ar*-4-nitrotetrahydroaceto- β -naphthalide at low temperatures. On hydrolysis it yields *ar*-3:4-dinitrotetrahydro- β -naphthylamine, long golden-yellow needles, m.p. 157° (Schroeter, &c., *l.c.*; Tetralin, G.m.b.H., D. R. P. 333157, 1916).

ar-Tetrahydro-1:2-naphthylenediamine is formed in a yield of 15 p.c. together with the alicyclic isomeride by the reduction of 1:2-naphthylenediamine with sodium and amyl alcohol (Bamberger and Schieffelin, Ber. 1889, 22, 1374); by the reduction of *ar*-1-nitrotetrahydro- β -naphthylamine in decahydronaphthalene solution with hydrogen in the presence of a catalyst; by the catalytic reduction of *ar*-1:2-dinitrotetrahydronaphthalene or its eutectic mixture with *ar*-1:3-dinitrotetrahydronaphthalene; by the stannous chloride reduction of *ar*-1:2-dinitrotetrahydronaphthalene; or by the hydrolysis of the product obtained by reducing *ar*-2-nitrotetrahydroaceto- α -naphthalide in ethereal solution by means of hydrogen in the presence of a catalyst (Schroeter, &c., *l.c.*). *ar*-Tetrahydro-1:2-naphthylenediamine crystallises in glistening leaflets or flat silky needles, m.p. 84°, b.p. 220°/81 mm. (Bamberger and Schieffelin), or m.p. 84°–85°, b.p. 172°–175°/13 mm. (Schroeter, &c.), has all the properties of an aromatic tetrahydro-base, and on oxidation with alkaline permanganate yields a mixture of adipic and oxalic acids; *dihydrochloride*, lustrous tabular crystals, m.p. about 260° (decomp.); *dinitrate*, silver-white satiny scales, m.p. 201°; 1-acetyl derivative, m.p. 149°–151°, *hydrochloride*, colourless needles; 1:2-diacetyl derivative, silky matted needles, m.p. 245° (Bamberger and Schieffelin), or 244°–245° (Schroeter, &c.). When condensed with phenanthrenequinone in alcoholic solution, the diamine forms *ar*-tetrahydronaphthylene-1:2-phenanthrazine, yellow felted needles, m.p. 228.5°–230°. *ac*-Tetrahydro-1:2-naphthylenediamine is formed together with the aromatic isomeride by the reduction of 1:2-naphthylenediamine in amyl alcoholic solution with sodium. It forms a *carbonate* and has all the properties of an alicyclic tetrahydro-base (Bamberger and Schieffelin, *l.c.*). *ar*-Tetrahydro-1:3-naphthylenediamine, pearly plates, m.p. 84°–85°, is prepared by reducing *ar*-1:3-dinitrotetrahydronaphthalene dissolved in tetrahydronaphthalene with hydrogen under pressure at 150°–160° in the presence of nickel; *ar*-3-aminotetrahydroaceto- α -naphthalide, m.p. 173°, is obtained by reducing the corresponding nitro-compound dissolved in tetrahydronaphthalene with hydrogen under 8–14 atmospheres pressure at 160° in the presence of a catalyst; *ar*-1-aminotetrahydroaceto-3-naphthalide, obtained by reducing an ethereal solution of *ar*-4-nitrotetrahydroaceto- β -naphthalide with hydrogen under a pressure of 10–12 atmospheres at 150° in the presence of a catalyst, forms colourless glistening needles, m.p. 110°–111°; *hydrochloride*, sparingly soluble in hydrochloric acid. The *ar*-1:3-diacetyl derivative, obtained by the further acetylation of either of the above monoacetyl derivatives or by the diacetylation of the tetra-

hydro-1:3-diamine, crystallises in small filamental needles, m.p. 245°–246°. *ar*-Tetrahydro-1:3-naphthylenediamine forms a *benzoyl derivative*, m.p. 235°, and a *benzylidene derivative*, m.p. 208°.

ar-Tetrahydro-2:3-naphthylenediamine, glistening leaflets, stable to light and air, m.p. 135°–136°, b.p. 165°/13 mm., is obtained by the reduction of *ar*-3-nitrotetrahydro- β -naphthylamine dissolved in decahydronaphthalene with hydrogen under pressure at 150° in the presence of a catalyst; *hydrochloride*, glistening leaflets; on boiling with acetic acid it forms *ar*-2-methyl-2:3-tetrahydronaphthiminazole, m.p. 251°–252°, and with phenanthrenequinone it yields *ar*-tetrahydronaphthylene-2:3-phenanthrazine, yellow glistening needles, m.p. 214°–216°.

ar-1:2:3-Triaminotetrahydronaphthalene, obtained by reducing either *ar*-3:4-dinitrotetrahydro- β -naphthylamine or *ar*-1:3-dinitrotetrahydro- β -naphthylamine with stannous chloride, is unstable in air, but forms a crystalline *hydrochloride* and a 1:2:3-triacetyl derivative, white microscopic needles, m.p. 285°.

ar-1:2:4-Triaminotetrahydronaphthalene, prepared by the stannous chloride reduction of *ar*-1:2:4-trinitrotetrahydronaphthalene or of *ar*-2:4-dinitrotetrahydro- α -naphthylamine, is also unstable, and yields a 1:2:4-triacetyl derivative, fine white needles, m.p. 315° (Schroeter, &c., *l.c.*; Tetralin, G.m.b.H., D. R. P. 333157, 1916).

ar-Tetrahydroethyl- β -naphthylamine, b.p. 291·5°/724 mm., a colourless, neutral mobile oil, volatile with steam, is formed to the extent of about 4 p.c. together with the alicyclic isomeride when ethyl- β -naphthylamine is reduced in amyl alcoholic solution with sodium. It forms an oily *nitrosoamine*; *hydrochloride*, clusters of long needles, m.p. 173·5°; *platinochloride*, small yellow needles slowly decomposed by cold water and immediately by hot water. *ar*-Tetrahydroethyl- β -naphthylamine on oxidation with alkaline permanganate yields adipic acid (Bamberger and Müller, Ber. 1889, 22, 1295). *ar*-Tetrahydro-diethyl- β -naphthylamine, colourless oil, b.p. 167°/16 mm., or 298°/709 mm., which rapidly becomes brown on exposure to air, is formed together with the alicyclic isomeride when diethyl- β -naphthylamine is reduced in amyl alcoholic solution with sodium (Bamberger and Williamson, Ber. 1889, 22, 1760). It does not react with formaldehyde under the conditions employed in the formation of 2:2'-tetraethyldiamino-1:1'-dinaphthylmethane, and in this respect it resembles an amine of the benzene series (Morgan, Chem. Soc. Trans. 1900, 77, 819). *ar*-Tetrahydro- β -naphthylamine also exhibits a benzenoid character when treated with formaldehyde, and there is no tendency towards the production of an acridine, but *methylene-ar-tetrahydro- β -naphthylamine*, (C₁₀H₁₁N:CH₂)₃, small white felted needles, m.p. 121°, is formed together with a *polymeride* of the anhydro-base, white powder darkening at 156° and melting at 164°–165°. The former does not form a benzoyl derivative, and on treatment with dilute acids, *ar*-tetrahydro- β -naphthylamine is regenerated. Trimolecular methylene-*ar*-tetrahydro- β -naphthylamine and its *polymeride* are interconvertible by solution in suitable solvents. *ar*-Tetrahydromethyl- β -naphthylamine, colourless oil, b.p. 267·5°/210 mm., is formed by reducing an amyl alcoholic solution

of methylene-*ar*-tetrahydro- β -naphthylamine with sodium; *hydrochloride*, white needles; *nitrate*, needles; *nitrosoamine*, yellow oil (Smith, Chem. Soc. Trans. 1904, 85, 732). *ar*-Tetrahydromethyl- β -naphthylamine, colourless mobile oil, b.p. 287°/718 mm., or 168°/695 mm., very similar in properties to *ar*-tetrahydroethyl- β -naphthylamine, is obtained together with small quantities of the isomeric alicyclic base when dimethyl- β -naphthylamine is reduced with sodium and amyl alcohol; *hydrochloride*, colourless very deliquescent crystals; *platinochloride*, yellow crystalline compound decomposed by boiling water; *ferrocyanide*, yellowish-white crystalline compound decomposed by boiling water; *picrate*, glistening needles. The base yields adipic acid when oxidised by permanganate (Bamberger and Müller, Ber. 1889, 22, 1295).

1-Methyl- β -naphthylamine, when reduced with sodium and amyl alcohol, yields *ar*-tetrahydro-1-methyl- β -naphthylamine, colourless liquid, b.p. 170°–175°/30 mm.; *acetyl derivative*, lustrous leaflets, m.p. 134°; *benzoyl derivative*, m.p. 222°, *hydrochloride*, colourless needles, m.p. 263°–264° (Mayer and Schnecko, Ber. 1923, 56, 1408).

ac-Tetrahydro- β -naphthylamine is obtained in a yield of 30–40 p.c., together with dihydronaphthalene, by treating an amyl alcoholic solution of β -naphthylamine with sodium, taking 12 grms. of sodium to 15 grms. of β -naphthylamine (Bamberger and Müller, Ber. 1888, 21, 847), or together with its aromatic isomeride if the amount of sodium be increased to 20 grms. (Bamberger and Kitchelt, Ber. 1890, 23, 876). The isomerides are separated by the conversion of the alicyclic compound into the carbonate. Attempts to increase the yield of the alicyclic tetrahydro-base by using such substances as cetyl alcohol, phenol, glycerol, amyl alcohol and vaseline were without result, and when valeric acid was used a little valeryl- β -naphthylamine was formed (Bamberger and Müller, *ibid.* 1888, 21, 1112). *ac*-Tetrahydro- β -naphthylamine is a colourless slightly viscid liquid with an intense ammoniacal pyridine-like odour, b.p. 162°/36 mm., or 249·5°/710 mm. with slight decomposition, sp.gr. 1·031 at 16° (Bamberger, Ber. 1887, 20, 2915; Bamberger and Müller, *ibid.* 1888, 21, 847), molecular rotation 16·147 (Perkin, Chem. Soc. Trans. 1896, 69, 1004). It is one of the strongest organic bases known, readily absorbing carbon dioxide from the air and displacing ammonia from its salts. It cannot be diazotised and does not yield azo-colouring matters with diazonium compounds. On oxidation with alkaline permanganate it yields a mixture of *o*-carboxy- β -phenyl-propionic acid and phthalic acid, and, when oxidised with potassium bichromate and sulphuric acid, it yields a mixture of phthalic acid, α -naphthol and α -naphthoquinone. The last two substances are independent oxidation products and are probably formed by the oxidation of dihydronaphthalene into which the base decomposes under certain conditions (Bamberger and Kitchelt, *l.c.*). On the other hand, oxidation with a neutral solution of Caro's acid yields the corresponding *oxime* (Bamberger and Seligman, Ber. 1903, 36, 709; cf. Bamberger and Lodter, Annalen, 1895, 288, 112; Bamberger and Voss, Ber. 1894, 27, 1547).

ac-Tetrahydro- β -naphthylamine forms a neutral *carbonate*, lustrous white needles;

hydrogen carbonate, white crystalline powder; *nitrite*, long silky needles or short strongly refractive prisms, m.p. 160° (decomp.) (Bamberger and Müller, Ber. 1888, 21, 847), which was shown by Noyes and Ballard (Ber. 1894, 27, 1450) to be a mixture of nitrite and nitrate, the pure nitrite melting at 137°; *hydrobromide*, pearly white tables; *hydrochloride*, silvery white tables, m.p. 237° (Bamberger and Müller), or 242°–243° (Noyes and Ballard); *nitrate*, tables, m.p. 210°–212° (Bamberger and Kirschelt, l.c.), or 215° (Noyes and Ballard); *sulphate*, lustrous white prisms; *bichromate*, orange-yellow prisms; *platinochloride*, orange-yellow prisms; *aurochloride*, golden-yellow needles; *picrate*, long golden-yellow needles; *ferrocyanide*, glistening needles (Bamberger and Müller, Ber. 1888, 21, 847); *acetate*, thick lustrous monoclinic prisms, m.p. 155·5°–156°, which effloresce (Bamberger and Kirschelt, l.c.). *ac-Tetrahydroaceto-β-naphthalide*, needles, m.p. 107·5°, is formed by the action of acetyl chloride on the base in benzene solution; *benzoyl derivative*, needles, m.p. 150°–151° (Bamberger and Müller, Ber. 1888, 21, 847); *benzylidene-ac-tetrahydro-β-naphthylamine*, crystallises in lustrous tables or prisms, m.p. 51·5°–52° (Bamberger and Kirschelt, l.c.). *ac-Tetrahydro-β-naphthylamine-ac-tetrahydro-β-naphthylthiocarbamate*, long lustrous needles, m.p. 142°, is obtained by treating a very dilute ethereal solution of the base at 0° with a very dilute ethereal solution of carbon disulphide, and yields on boiling in alcoholic solution *bis-ac-tetrahydro-β-naphthylthiocarbamide*, stellate groups of white lustrous needles, m.p. 166·5°; *ac-tetrahydro-β-naphthylthiocarbamide* forms glassy prisms, m.p. 161° (decomp.); *ac-tetrahydro-β-naphthylphenylcarbamide* crystallises in clusters of long silky needles, m.p. 165·5° (Bamberger and Müller, Ber. 1888, 21, 847). When treated with diazobenzene chloride, *ac-tetrahydro-β-naphthylamine* yields an explosive *diazoamino-derivative*, a weak base, volatile with steam; *picrate*, m.p. 118° (Bamberger and Müller, *ibid.* 1112).

ar-Tetrahydro-β-naphthonitrile, m.p. 20°–21°, b.p. 151°–152°/11 mm., is obtained from *ar-tetrahydro-β-naphthylamine* by the Sandmeyer reaction. The tetrahydronitrile is reduced by sodium and ethyl alcohol to *ar-tetrahydro-β-naphthylmethylaniline*, colourless liquid, b.p. 146°–148°/11 mm.; *hydrochloride*, m.p. 248°; *picrate*, m.p. 215°; *benzoyl derivative*, long needles, m.p. 165°, b.p. 260°–265°/10 mm.; *p-nitrobenzoyl derivative*, m.p. 170°; *phenylthiocarbamide*, m.p. 130°. The above methylaniline may be prepared more conveniently in 90 p.c. yield by the reduction of *β-naphthylmethylaniline* with sodium and amyl alcohol, but it appears to be contaminated with traces of *ac-tetrahydro-β-naphthylmethylaniline* (von Braun, Moldaenke, Dirlam and Gruber, Ber. 1922, 55, 1700). The catalytic reduction of *ar-tetrahydro-β-naphthonitrile* in tetrahydronaphthalene solution also gives rise to *ar-tetrahydro-β-naphthylmethylaniline*, together with *bis-ar-tetrahydro-β-naphthylmethylaniline*, b.p. 265°–267°/11 mm. (*hydrochloride*, m.p. 245°; *benzoyl derivative*, m.p. 241°–242°; *nitroso-derivative*, m.p. 76°) (von Braun, Blessing and Zobel, Ber. 1923, 56, 1988).

When *β-naphthonitrile* in alcoholic solution

is reduced with sodium, the main products are dihydronaphthalene and *ac-tetrahydro-β-naphthylmethylaniline*, a colourless non-fluorescent liquid, b.p. 270·2°/729 mm., with an odour similar to that of the *α*-isomeride, but hydrogen cyanide, ammonia, *β-naphthoic acid*, and frequently *β-naphthamide* are formed as by-products. *ac-Tetrahydro-β-naphthylmethylaniline* is a strong base which absorbs carbon dioxide from the air; *hydrochloride*, tufts of needles, m.p. 228·5°–229°; *platinochloride*, small lustrous yellow needles; *sulphate*, long thin prisms; *picrate*, yellow needles. *ac-Phenyl-tetrahydro-β-naphthylmethylethylcarbamide* forms colourless needles, m.p. 141°; the corresponding *thiocarbamide*, colourless rosettes, m.p. 139·5°–140°; *ac-tetrahydro-β-naphthylmethylethylcarbamide*, colourless plates, m.p. 135°–135·5°; *bis-ac-tetrahydro-β-naphthylmethylethylcarbamide*, satiny plates, m.p. 225·5°–226°; *ac-tetrahydro-β-naphthylmethylaniline-ac-tetrahydro-β-naphthylmethyl dithiocarbamate*, vitreous needles, m.p. 128° (decomp.); *bis-ac-tetrahydro-β-naphthylmethylthiocarbamide*, nacreous plates, m.p. 142·5°–143°; *acetyl-ac-tetrahydro-β-naphthylmethylaniline*, long needles, m.p. 64°–65° (Bamberger and Helwig, Ber. 1889, 22, 1912; Bamberger and Boekmann, Ber. 1887, 20, 1711).

ac-Tetrahydro-β-naphthylamine is converted by *α-ε*-dibromopentane into *ac-2-piperidinotetrahydronaphthalene*, colourless liquid, b.p. 186°–187°/16 mm., which forms a *hydrochloride*, m.p. 230°–231°; a *hydrobromide*, m.p. 233°–234°; a *methiodide*, m.p. 209°, and a *picrate*, m.p. 203°–204°. Both the piperidino-compound and its *α*-isomeride undergo fission with cyanogen bromide, but the production of bromotetrahydronaphthalene is much more marked with the *α*-than with the *β*-isomeride (von Braun, Braunsdorf and Kirschbaum, Ber. 1922, 55, 3648).

Ethyl cyanoacetate reacts in the cold with *ac-tetrahydro-β-naphthylamine* to yield *ac-cyanoacetotetrahydro-β-naphthylamide*, long colourless needles, m.p. 175°–176°, which, when oxidised with potassium permanganate, yields *ac-tetrahydro-β-naphthylloxamic acid*, small crystals, m.p. 163°–164°, whilst if the alicyclic tetrahydro-base is treated first with acetone and then with ethylcyanoacetate *1-ac-tetrahydro-β-naphthyl-3-cyanotrimethyl-piperidone*, long needles, m.p. 210°–211°, is obtained (Benedicenti, Ann. Chim. Farm. 22, 433). The exhaustive methylation of *ac-tetrahydro-β-naphthylamine* yields quantitatively the quaternary ammonium salt, the *methiodide*, swallow-tailed twin crystals, m.p. 228°, from which the *ammonium base* is obtained by shaking with freshly precipitated silver oxide. The product on distillation *in vacuo* yields pure dihydronaphthalene (Willstätter and King, Ber. 1913, 46, 527) which was shown to be Δ^1 - or 1:2-dihydronaphthalene by Straus (Ber. 1913, 46, 1051). When *ac-tetrahydro-β-naphthyltrimethylammonium chloride* is distilled, *ac-tetrahydrodimethyl-β-naphthylamine* is formed (Waser, Ber. 1916, 40, 1202); it is also obtained in very small quantities, together with the aromatic isomeride, by the sodium and alcoholic reduction of dimethyl-*β-naphthylamine* (Bamberger and Müller, Ber. 1889, 22, 1295). *ac-Tetrahydrodimethyl-β-naphthylamine* is a colourless mobile oil, b.p. 132·3°–133·3°/11 mm.

(Waser), or 116°/22 mm. (Bamberger and Müller). It resembles the ethyl base in all its properties, and its physiological action is similar to, but stronger than, that of ac-tetrahydro- β -naphthylamine; *hydrochloride*, needles (Bamberger and Müller), or silky leaflets, m.p. 214°–215° (decomp.) (Waser); *platinochloride*, orange-red needles, m.p. 210° (decomp.).

ac-Tetrahydromethyl- β -naphthylamine, obtained by the action of methyl sulphate on the hydro-base, is a mobile oil, b.p. 118°–119·8°/9 mm.; d_4^{20} 1·024; *hydrochloride*, sinters at 196° and melts at 214°; *platinichloride*, m.p. 228° (decomp.) (Waser, *l.c.*). *ac-Tetrahydroethyl- β -naphthylamine*, colourless mobile oil, b.p. 267°/724 mm., or 153°/23 mm., readily volatile with steam, with an ammoniacal pyridine-like odour, is obtained in a yield of 35–40 p.c., together with its aromatic isomeride, when ethyl- β -naphthylamine in amyl alcoholic solution is reduced with sodium. It is strongly alkaline, has a marked affinity for carbon dioxide forming a carbonate, and possesses the physiological properties of alicyclic β -tetrahydro-bases. It forms a *hydrochloride*, clusters of glistening prisms, m.p. 223·5°; *nitrate*, long glistening needles, or silvery plates, m.p. 184°; *nitrite*, long silky needles not decomposed by boiling water, m.p. 180°; *picrate*, large orange-red needles or glistening rosettes, m.p. 183·5°; *platinochloride*, orange-yellow stellate crystals, m.p. 204°; *oxalate*, flaky needles; *carbonate*, deliquescent glistening needles; *acetate*, a syrup; *acetyl derivative*, colourless oil, b.p. 328°/718 mm.; *nitrosoamine*, yellowish oil very slightly volatile with steam. *Diazobenzene-ac- β -ethylamino-tetrahydronaphthalene*, sulphur-yellow hexagonal plates, m.p. 58°, forms a *picrate*, ruby-red needles, which decomposes on exposure to light or when heated at about 100° (Bamberger and Müller, Ber. 1889, 22, 1295). *ac-Tetrahydro- β -naphthylethyl carbamate*, obtained by the action of an ethereal solution of ethyl chloroformate on ac-tetrahydro- β -naphthylamine, forms rosettes of needles, m.p. 82°, whilst the latter on treatment with an ethereal solution of ethyl isocyanate is converted quantitatively into *ac-tetrahydro- β -naphthylethylthiocarbamide*, four-sided prisms, m.p. 131·5° (Waser, *l.c.*).

ac-Tetrahydrodiethyl- β -naphthylamine, an oil with all the properties of an alicyclic tetrahydro-base, is obtained in a very low yield, together with the aromatic isomeride by the reduction of diethyl- β -naphthylamine in amyl alcoholic solution with sodium; *carbonate*, snow-white deliquescent needles; *hydrochloride*, thin lustrous prisms (Bamberger and Williamson, Ber. 1889, 22, 1760).

ac-Tetrahydro-p-tolyl- β -naphthylamine, colourless plates, m.p. 44°, b.p. 93°/18 mm., is exceedingly volatile and has a piperidine-like odour, together with a distinct odour of narcissus (Bamberger and Müller, *l.c.*).

Hydroxy-derivatives of tetrahydronaphthalene.—*ar-Tetrahydro- α -naphthol* (α -Tetralol) is the sole reduction product of α -naphthol using sodium and amyl alcohol (Bamberger and Bordt, Ber. 1890, 23, 215), although a large excess of sodium is required for complete reduction (Jacobson and Turnbull, Ber. 1898, 31, 890), and is identical with the product obtained from

ar-tetrahydro- α -naphthylamine by means of the dizao-reaction (Bamberger and Althausse, Ber. 1888, 21, 1892); it is also obtained in 80 p.c. yield from *ar-tetrahydronaphthalene- α -sodium sulphonate* by fusion with about 4 parts of 70 p.c. potassium hydroxide at 280°. In the latter case, the product is precipitated with carbon dioxide and distilled *in vacuo* (Schroeter, Svanoe, Einbeck, Geller and Riebensahm, Annalen, 1922, 426, 83).

Brochet and Cornubert (Compt. rend, 1921, 172, 1499; Bull. Soc. chim. 1922, (iv.) 31, 1280) state that both α - and β -naphthol yield a mixture of aromatic and alicyclic tetrahydro-derivatives when hydrogenated under pressure in presence of reduced nickel, the latter isomeride being formed in the greater quantity, but Schroeter (*l.c.*; Schroeter and Tetralin, G.m.b.H., D. R. P. 352720, 1920) found that the catalytic reduction of α -naphthol for the preparation of *ar-tetrahydro- α -naphthol* can only be used under very specified conditions. Thus, if a solution of pure α -naphthol be treated at 200° with hydrogen in the presence of a nickel-containing catalyst, two molecular proportions of hydrogen are absorbed, but the reaction product only contains about 25–30 p.c. of *ar-tetrahydro- α -naphthol*, the greater portion of the α -naphthol being converted into tetrahydronaphthalene together with about 10 p.c. of ac- α -ketotetrahydronaphthalene (α -Tetralon). On the other hand, when the temperature is reduced to a minimum so that not more than one molecular proportion of hydrogen is absorbed, the main product is ac- α -ketotetrahydronaphthalene, and the *ar-tetrahydro- α -naphthol*, formed simultaneously, still contains unaltered α -naphthol (*cf.* Komatsu and Nodzu, Mem. Coll. Sci. Kyoto, 1923, 6, 177; Komatsu and Kumamoto, *ibid.* 1924, 7, 135).

ar-Tetrahydro- α -naphthol forms silvery-white tables or monoclinic plates, m.p. 68·5°–69°, b.p. 264·5°–265·5°/705 mm. (Bamberger and Bordt), or 147°/14 mm. (Schroeter, etc.); for the ultra-violet absorption spectra, see Komatsu, Masumoto and Kumamoto (Mem. Coll. Sci. Kyoto, 1924, 7, 287); *ethyl ether*, viscid heavy oil, b.p. 259°/705 mm.

In contrast with benzene-azo- α -naphthylethyl ether, which readily yields an *o*-semidine but no *p*-semidine, benzene-azo-*ar-tetrahydro- α -naphthyl ethyl ether* yields a considerable quantity of the *p*-semidine, whilst the *o*-semidine amounts to only 52 p.c. of the total semidines produced. The hydrogenated ring of the naphthalene nucleus thus exerts an influence similar to that of a methyl group in the *o*-position with respect to the azo group in a benzenoid analogue.

*Benzene-azo-*ar-tetrahydro- α -naphthyl ethyl ether**, obtained by the action of sodium ethoxide and ethyl iodide on the corresponding tetrahydro-naphthol derivative, forms orange-red prisms with a golden lustre, m.p. 91·5°. On reduction it yields the *o*- and *p*-semidine derivatives, as well as small amounts of *p-amino-*ar-tetrahydro- α -naphthyl ethyl ether**, long colourless needles, m.p. 60°, which is also obtained by ethylating 4-benzene-azo-*ar-tetrahydro- β -naphthol* and reducing the product catalytically in tetrahydronaphthalene solution (Schroeter, &c., *l.c.*).

The *o*-semidine derivative, *ar-4-amino-3-*

anilino-1-ethoxy-tetrahydronaphthalene, forms colourless plates or needles, which become pink on exposure to air and melt at 168°–169°. The corresponding *azimide* crystallises in colourless oblique tablets, m.p. 125°–126°; the *stilbazonium base* forms yellow prisms, m.p. 151.5°; the *methenyl compound*, obtained by heating the base with formic acid, forms thin plates, m.p. 139°; the *carbon disulphide derivative* is only formed slowly and melts at 269°–270°; the *o-hydroxy-benzylidene derivative*, prepared by the use of salicyl aldehyde, crystallises in yellow prisms, m.p. 130°–131°. The *o-semidine* is oxidised by ferric chloride to *ar-anilinotetrahydro- α -naphthaquinone*, brownish-red crystals, m.p. 164°. The *p-semidine derivative*, *ar-4-p-aminophenyl-1-ethoxytetrahydro- α -naphthylamine*, crystallises in colourless prisms, m.p. 87°–88°, and becomes bluish on exposure to air; the *sulphate* is very sparingly soluble in water, whilst the *hydrochloride* dissolves more readily; the *monoacetyl derivative* forms colourless needles, m.p. 177°–178°, whilst the *thiocarbamide* crystallises in plates, m.p. 201° (Jacobson and Turnbull, *l.c.*).

Ethyl- α -naphthyl acetate, on reduction with sodium and absolute alcohol, yields *tetrahydronaphthylethanol*, b.p. 187°/25 mm. (*phenylurethane*, m.p. 91°), and *ethyltetrahydronaphthyl acetate* (free acid, m.p. 131°). Primary α -naphthylethanol, under similar conditions, yields a *dihydronaphthylethanol*, b.p. 190°/22 mm. (*phenylurethane*, m.p. 106°), whilst secondary α -naphthylethanol yields *ethyldihydronaphthalene*, b.p. 240°/760 mm. (de Pommereau, *Compt. rend.* 1922, 175, 105; *Bull. Soc. chim.* 1922, 33, 689).

ar-Tetrahydro- α -naphthol 4-sulphonic acid, sodium salt, colourless prismatic needles, is obtained by the action of cold concentrated sulphuric acid on *ar-tetrahydro- α -naphthol*, but unlike α -naphthol 4-sulphonic acid, cannot be obtained by the action of sodium hydrogen sulphite on sodium-*ar-tetrahydro- α -naphthylamine 4-sulphonate*, nor by boiling the diazo-compound of this amino-sulphonic acid, owing to the ease with which the sulphonic group is hydrolysed with formation of *ar-tetrahydro- α -naphthol*. The sulphonic acid, in neutral or alkaline solution, does not couple with diazonium salts.

ar-2-Nitrotetrahydro- α -naphthol-4-sulphonic acid, long pale yellow flat needles, m.p. 182°, is obtained by nitrating the sulphonic acid in sulphuric acid solution with one molecular proportion of nitric acid, sp.gr. 1.4. On hydrolysis with dilute sulphuric acid it yields *ar-2-nitro-tetrahydro- α -naphthol*, long yellow needles, volatile with steam, m.p. 56°; *ar-2:4-dinitro-tetrahydro- α -naphthol*, large yellow rhombic prisms, slightly volatile with steam, m.p. 105° (Green and Rowe, *Chem. Soc. Trans.* 1918, 113, 955).

The product obtained by the action of nitrous acid on *ar-tetrahydro- α -naphthol* was believed by Green and Rowe to be the 4-nitro-derivative, but it has been shown by Schroeter (*l.c.*) that it is actually *ar-4-nitrosotetrahydro- α -naphthol*, yellow needles, m.p. 163° (Green and Rowe), or 161°–163° (Schroeter, &c.).

ar-4-Aminotetrahydro- α -naphthol, colourless needles, m.p. 146°–147°, b.p. 208°–210°/10 mm.,

is obtained by reducing *ar-4-nitrosotetrahydro- α -naphthol* with stannous chloride, and is identical with the product obtained by reducing with sodium hydrosulphite the azo compound derived from *ar-tetrahydro- α -naphthol* and diazotised sulphanilic acid. *ar-2-Aminotetrahydro- α -naphthol*, m.p. 110°–111°, is obtained readily by reducing *ar-2-nitrotetrahydro- α -naphthol*; its *hydrochloride* on heating with urea to 200° yields a *carbonyl derivative*, m.p. 205°, which is identical with the product obtained when *ar-tetrahydro- α -naphthol-2-carboxylazide*, m.p. 84°, is heated in toluene solution. *ar-3-Acetylaminotetrahydro- α -naphthol*, colourless needles, m.p. 211°, is prepared from *ar-3-acetyltetrahydro-1:3-naphthylenediamine* by means of the diazo-reaction. On hydrolysis, it yields *ar-3-aminotetrahydro- α -naphthol*, white leaflets, m.p. 197°; *hydrochloride*, colourless needles. *ar-Tetrahydro- α -naphthol 3-carboxylic acid*, m.p. 165°–166°, is obtained by the action of carbon dioxide under pressure on *ar-tetrahydro- α -naphthol* in presence of potassium carbonate; sodium salt, leaflets; *acetyl derivative*, m.p. 170°; *methyl ester*, obtained by direct methylation, melts at 56°, b.p. 190°/16 mm.; *hydrazide*, obtained by treating the methyl ester with hydrazine hydrate in alcoholic solution, melts at 205° when heated quickly. The hydrazide, on treatment with acetone, yields the corresponding *isopropylidenehydrazone*, m.p. 136°, and on treating with nitrous acid in alcoholic-acetic acid solution yields *ar-tetrahydro- α -naphthol-2-carboxylazide*, m.p. 84° (Schroeter, &c., *l.c.*).

ac-Tetrahydro- α -naphthol, oil, b.p. 132°–134°/12–13 mm., or b.p. 139°–140°/17 mms. (corr.), d_4^{17} 1.0896, n_D^{17} 1.5671, can be obtained by reducing *ac- α -ketotetrahydronaphthalene* with sodium and absolute alcohol, or sodium and moist ether. It forms a *phenylurethane*, m.p. 121°–122°, which decomposes quantitatively into carbon dioxide, aniline, and Δ^1 -dihydronaphthalene when heated (Schroeter, &c., *l.c.*; Straus and Lemmel, *Ber.* 1921, 54, 25).

ar-Tetrahydro- β -naphthol is formed in small yield, together with its alicyclic isomeride, by the reduction of β -naphthol with sodium and amyl alcohol (Bamberger and Kitschelt, *Ber.* 1890, 23, 885), and is identical with the product obtained from *ar-tetrahydro- β -naphthylamine* by means of the diazo-reaction (*ibid.* 876). It is also formed together with its alicyclic isomeride and phenylene-acetic-propionic acid during the reduction of 2-hydroxy- α -naphthoic acid with sodium and ethyl alcohol (Einhorn and Lumsden, *Annalen*, 1895, 286, 257). Schroeter (*l.c.*; Schroeter and Schrauth, *D. R. P.* 299603, 1916; Eng. Pat. 148408, 1920) prepared *ar-tetrahydro- β -naphthol* in a yield of 75–80 p.c. by fusing *ar-tetrahydronaphthalene 2-sulphonic acid* for 2½–3 hours at 280° with 75 p.c. caustic alkali solution. The product is precipitated by carbon dioxide from an aqueous solution of its alkali salt, followed by distillation with superheated steam under reduced pressure. The *tetrahydro- β -naphthol* thus obtained is not pure, but may be purified by conversion into the sulphonic acid, followed by the removal of the sulphonic group, and crystallisation from sulphuric acid, or better from light petroleum. The reduction of β -naphthol by means of

hydrogen in the presence of a catalyst yields a somewhat similar result to that obtained by the sodium and amyl alcohol method, ac-tetrahydro- β -naphthol being formed in the greater quantity. There is, however, a noteworthy difference between the behaviour of α - and β -naphthol on catalytic reduction, for no tetrahydronaphthalene or ac- β -ketotetrahydronaphthalene is obtained by the cautious or incomplete reduction of β -naphthol. This difference in behaviour is to be explained by the fact that α -naphthol yields primarily ac- Δ^1 - or 3:4-dihydro- α -naphthol, which readily passes into the saturated and relatively stable ac- α -ketotetrahydronaphthalene, whereas β -naphthol yields primarily ac- Δ^3 - or 1:2-dihydro- β -naphthol, which cannot isomerise into a keto-form, and is further reduced to ac-tetrahydro- β -naphthol, a little ar-tetrahydro- β -naphthol also being formed during the reduction (Schroeter, etc., *l.c.*; Schroeter and Tetralin, G.m.b.H., D. R. P. 352720, 1920; Brochet and Cornubert, Bull. Soc. chim. 1922, (iv.) 31, 1280).

By adding water slowly to a mixture of sodium and a solution of β -naphthyl ethyl ether in solvent naphtha at 145° tetrahydro- β -naphthyl ethyl ether, oil, b.p. 158°/28 mm., is obtained, identical with the product of the ethylation of tetrahydro- β -naphthol (Chem. Fabr. Griesheim-Elektron, D. R. P. 370974).

ar-Tetrahydro- β -naphthol crystallises in lustrous needles, m.p. 61·5°–62·5°, b.p. 148°/12 mm. (Schroeter, &c., *l.c.*), or m.p. 58°, b.p. 275°/707 mm. (Bamberger and Kirschelt, *l.c.*); for the ultra-violet absorption spectra, see Komatsu, Masumoto and Kumamoto (Mem. Coll. Sci. Kyoto, 1924, 7, 287). It exhibits the reactions of a phenol, and resembles ar-tetrahydro- α -naphthol in its properties. On treatment with acetic anhydride it forms an acetate, a rather viscous oil, b.p. 158°/14 mm., and with benzoyl chloride in pyridine solution it forms a benzoate, colourless prisms, m.p. 96°, b.p. 220°–222°/10 mm.

ar-Tetrahydro- β -naphthol 3-sulphonic acid, colourless needles + 2H₂O, m.p. 92°, is obtained by warming a mixture of equal weights of ar-tetrahydro- β -naphthol and concentrated sulphuric acid on the water-bath until there is no precipitate on dilution with water. It forms a sparingly soluble sodium salt, and a barium salt. It is hydrolysed on boiling with hydrochloric acid with formation of ar-tetrahydro- β -naphthol.

ar-1-Bromotetrahydro- β -naphthol, m.p. 74°, b.p. 160°/13 mm., is obtained by the direct bromination of ar-tetrahydro- β -naphthol, and on sulphonation yields ar-1-bromotetrahydro- β -naphthol 3-sulphonic acid, which is obtained also by the bromination of ar-tetrahydro- β -naphthol 3-sulphonic acid in sulphuric acid solution. The sulphonic group is removed readily by hydrolysis with hydrochloric acid. ar-1:3-Dibromotetrahydro- β -naphthol, colourless crystals, m.p. 37°, b.p. 198°–200°/15 mm., is obtained by dibrominating ar-tetrahydro- β -naphthol in carbon tetrachloride solution, or by the bromination of aqueous solutions of ar-tetrahydro- β -naphthol 3-sulphonic acid, or ar-1-bromotetrahydro- β -naphthol 3-sulphonic acid, when the sulphonic group is replaced by bromine. It is characterised by a well crystalline acetate, m.p.

87°, from which the dibromotetrahydro- β -naphthol can be regenerated by hydrolysis with alcoholic potassium hydroxide. ar-1-Bromo-3-nitrotetrahydro- β -naphthol, long yellow needles, m.p. 129°, is prepared by nitrating ar-1-bromo-tetrahydro- β -naphthol 3-sulphonic acid, the sulphonic group being replaced by the nitro-group; sodium salt, red leaflets. ar-1-Chloro-3-nitrotetrahydro- β -naphthol, yellow needles, m.p. 96°, is obtained by chlorinating ar-tetrahydro- β -naphthol 3-sulphonic acid and treating the crude product with nitric acid, the nitro-group replacing the sulphonic group. When ar-1-bromo-3-nitrotetrahydro- β -naphthol is suspended in ether, and reduced with stannous chloride dissolved in ether saturated with hydrogen chloride, a mixture of ar-1-bromo-3-amino-tetrahydro- β -naphthol and ar-3-aminotetrahydro- β -naphthol is formed. ar-1-Bromo-3-aminotetrahydro- β -naphthol crystallises from 70 p.c. alcohol or toluene in needles, m.p. 127°, and forms a sulphate, nitrate, and hydrochloride, which are sparingly soluble in water. ar-3-Aminotetrahydro- β -naphthol crystallises from absolute alcohol in leaflets, m.p. 202°, and forms a hydrochloride and nitrate, readily soluble in water, whilst the sulphate is only sparingly soluble in cold water. ar-3-Aminotetrahydro- β -naphthol is obtained also by heating carbonyl-3-amino-ar-tetrahydro- β -naphthol with concentrated hydrochloric acid for 6 hours at 170°. ar-Carbonyl-3-aminotetrahydro- β -naphthol, colourless crystals, m.p. 196°, is formed by boiling ar-tetrahydro- β -naphthol-3-carboxyl-azide with toluene under a reflux.

The piperonyl derivative of ar-3-aminotetrahydro- β -naphthol, yellow crystals, m.p. 160°, is obtained in almost quantitative yield by the addition of a hot concentrated solution of piperonal to a hot alcoholic solution of ar-3-aminotetrahydro- β -naphthol. ar-1-Aminotetrahydro- β -naphthol, colourless leaflets, m.p. 148°, is obtained by reducing benzene-azo-ar-tetrahydro- β -naphthol, m.p. 84°, with stannous chloride or sodium hydrosulphite. When diazobenzene chloride is coupled with ar-tetrahydro- β -naphthol an isomeric benzene-azo-ar-tetrahydro- β -naphthol, m.p. 110°, is formed occasionally, which on reduction with stannous chloride yields an ar-aminotetrahydro- β -naphthol, m.p. 173°. The carbonyl derivative of the latter compound, obtained by heating its hydrochloride with urea to 200°, forms reddish needles, m.p. 188°, whilst the carbonyl derivative of ar-1-aminotetrahydro- β -naphthol, prepared in a similar manner, melts at 189°–190°.

ar-4-Acetylaminotetrahydro- β -naphthol, colourless needles, m.p. 222°, is obtained readily from ar-4-acetylaminotetrahydro- β -naphthylamine by the diazo reaction, and on hydrolysis with fuming hydrochloric acid yields ar-4-aminotetrahydro- β -naphthol, colourless leaflets, m.p. 177°; hydrochloride, sparingly soluble in cold water. The latter compound is not identical with the previously mentioned ar-amino-tetrahydro- β -naphthol, m.p. 173°, of unknown orientation. ar-1:3-Dinitrotetrahydro- β -naphthol, yellow needles, m.p. 141°, is obtained by warming a mixture of nitric acid, sp.gr. 1·4, and ar-tetrahydro- β -naphthol 3-sulphonic acid dissolved in dilute sulphuric acid; the sodium salt, orange-red needles, and the potassium salt,

orange-red needles, both turn brick-red on drying at 100°–105°, and decompose with explosive violence at 180°–190°; *ammonium salt*, citron-yellow needles; the *barium* and *lead salts*, both of which are yellow powders, do not explode nor change their colour on heating. An ethereal solution of *ar-1:3-dinitrotetrahydro-β-naphthol*, when reduced with an ethereal solution of stannous chloride which has been saturated with hydrogen chloride, yields *ar-1-nitro-3-amino-tetrahydro-β-naphthol*, copper-coloured needles, m.p. 127°; *hydrochloride*, yellow leaflets. *ar-1:3-Diaminotetrahydro-β-naphthol*, colourless leaflets, m.p. 214°–216° (decomp.), is obtained, on the other hand, when *ar-1:3-dinitrotetrahydro-β-naphthol* is reduced similarly in alcoholic solution. When *ar-tetrahydro-β-naphthol* is heated to 160° for 5–6 hours with carbon dioxide under a pressure of 10 atmospheres in the presence of potassium carbonate, *potassium ar-tetrahydro-β-naphthol 3-carboxylate* is formed, from which the free *acid* is obtained as a white powder, m.p. 182°. *ar-Tetrahydro-β-naphthol 3-carboxylic acid* is best purified by conversion into the methyl ester, which is then distilled and hydrolysed; *methyl ester*, m.p. 42°, b.p. 179°/15 mm.; *ethyl ester*, liquid, b.p. 179°/13 mm. Hydrazine converts the methyl ester of *ar-tetrahydro-β-naphthol 3-carboxylic acid* into a *hydrazide*, m.p. 146°, which readily condenses with acetone to form an *isopropylidene hydrazone*, m.p. 235°. On treatment with nitrous acid the hydrazide yields *ar-tetrahydro-β-naphthol 3-carboxylazide*, long colourless needles, m.p. 99°–100°, which on heating above its melting-point decomposes violently with evolution of nitrogen and formation of the carbonyl derivative of *ar-3-amino-tetrahydro-β-naphthol* previously mentioned. *ar-Tetrahydro-β-naphthol 3-carboxylic acid* forms an *anilide*, m.p. 182°–184°; an *acetyl derivative*, m.p. 142°–143°, and on treatment with nitric acid in glacial acetic acid solution yields *ar-1-nitrotetrahydro-β-naphthol 3-carboxylic acid*, yellow needles, m.p. 200°–202°. The latter on reduction in ethereal solution with hydrogen under 20 atmospheres pressure in the presence of a nickel catalyst yields *ar-1-amino-β-naphthol 3-carboxylic acid*, colourless prisms, m.p. 208°–210°; *diacetyl derivative*, m.p. 180°–181°. *ar-2-Methoxytetrahydronaphthalene*, an oil, b.p. 129°–131°/11 mm., obtained by the action of dimethyl sulphate on *ar-tetrahydro-β-naphthol*, on sulphonation yields *ar-2-methoxytetrahydronaphthalene 3-sulphonic acid*, m.p. 107°. *ar-2-Methoxy-3-nitro-1-bromotetrahydronaphthalene*, yellow needles, m.p. 64°, is obtained by methylating *ar-1-bromo-3-nitro-tetrahydro-β-naphthol*, and on reduction with stannous chloride yields *ar-2-methoxy-3-amino-1-bromotetrahydronaphthalene*, an oil which crystallises on keeping; *sulphate*, long white needles + 4H₂O. *ar-2-Methoxy-3-piperonylideneamino-tetrahydronaphthalene*, colourless crystals, m.p. 120°, on hydrolysis with hydrochloric acid yields *ar-2-methoxy-3-aminotetrahydronaphthalene*, large leaflets, m.p. 86°.

ar-2-Methoxy-1-aminotetrahydronaphthalene, m.p. 64°, b.p. 195°–200°/20 mm., is formed by reducing 2-methoxy-1-aminonaphthalene (m.p. 54°) with sodium and amyl alcohol, and on hydrolysis with concentrated hydrochloric acid at 180°–190° it yields *ar-1-aminotetrahydro-β-*

naphthol, m.p. 148°. *ar-2-Methoxy-1:3-dinitrotetrahydronaphthalene*, colourless crystals, m.p. 86·5°, is obtained by heating a mixture of dry sodium *ar-1:3-dinitrotetrahydronaphtholate* and dimethyl sulphate in toluene suspension for 5 hours, and is not formed by the action of dimethyl sulphate on an alkaline solution of the dinitrotetrahydronaphthol. *ar-2-Methoxy-1-nitro-3-aminotetrahydronaphthalene*, m.p. 117°, is obtained by reducing the corresponding dinitro-compound with stannous chloride in ethereal solution, whereas if the reduction with stannous chloride be effected in alcoholic solution, or in tetrahydronaphthalene solution, at 120° by means of hydrogen under pressure *ar-2-methoxy-1:3-diaminotetrahydronaphthalene*, prisms, m.p. 89°, is formed (Schroeter, &c., *l.c.*; Tetralin, G.m.b.H., D. R. P. 357663, 1917).

ar-Tetrahydro-β-naphthylxyethylmethyl-aniline, m.p. 52°–53°, b.p. 257°–258°/14 mm., is obtained by treating *ar-tetrahydro-β-naphthol* with *N-β-bromoethylmethyl-aniline*; *picrate*, m.p. 122°; *hydrochloride*, m.p. 163°; *methiodide*, colourless crystalline powder, m.p. 123°. *ar-Tetrahydro-β-naphthylvinyl ether*, b.p. 121°–122°/11 mm., has a faint, but not unpleasant odour, less marked than that of the corresponding *allyl ether*, b.p. 158°–161°/23 mm. (von Braun and Kirschbaum, Ber. 1920, 53, 1403).

On reduction with sodium and amyl alcohol, *β-dinaphthylene oxide* yields *tetrahydro-β-dinaphthylene oxide*, glistening leaflets or colourless needles, m.p. 168°; *dibromotetrahydro-β-dinaphthylene oxide*, m.p. 137° (Hönigschmid, Monatsh. 1901, 22, 561; 1902, 23, 829).

ac-Tetrahydro-β-naphthol is the main hydrogenation product (30 p.c. yield) obtained by the addition of sodium to a boiling amyl alcoholic solution of *β-naphthol* (Bamberger and Lodter, Ber. 1890, 23, 197); it is also formed by reducing *Δ¹-dihydronaphthalene oxide* or *Δ¹-dihydronaphthalene bromohydrin* in moist ethereal solution with sodium (Straus and Rohrbacher, Ber. 1921, 54, 40); and by the reduction of *β-naphthol* with hydrogen under 15 atmospheres pressure in the presence of reduced nickel (Brochet and Cornubert, Compt. rend. 1921, 172, 1499; Bull. Soc. chim. 1922, (iv) 31, 1280; cf. Einhorn and Lumsden, Annalen, 1895, 286, 257), or a nickel containing catalyst (Schroeter, &c., Annalen, 1922, 426, 89). *ac-Tetrahydro-β-naphthol* is a colourless, transparent, extremely viscid, non-fluorescent oil with an odour of sage, b.p. 264°/716 mm., or 176·5°–178°/53 mm., or 144·5°–145·6°/20 mm. (corr.), d_4^{17} 1·0715, n_D^{17} 1·5523; *phenylurethane*, m.p. 99°. It is insoluble in alkalis, does not condense with diazonium salts, and on oxidation with permanganate yields *o-carboxy-β-phenylpropionic acid*, whilst when warmed with solid potassium hydroxide it yields dihydronaphthalene. When an ethereal solution of *ac-tetrahydro-β-naphthol* is treated with sodium, it behaves like an alcohol, hydrogen is liberated, and a *sodium derivative* is formed. *Sodium ac-tetrahydro-β-naphthyl carbonate*, a very unstable white gelatinous compound, is formed by passing carbon dioxide through a well-cooled ethereal solution of the above sodium derivative. *ac-Tetrahydro-β-naphthyl acetate* is a pale yellow, extremely viscid oil of fruity odour, which boils

at 169°/34 mm., or 268°–280°/atm. with partial decomposition into acetic acid and Δ^1 -dihydronaphthalene; the *chloride* and *iodide* similarly decompose on distillation into Δ^1 -dihydronaphthalene and the corresponding acid; *benzoate*, lustrous tablets, m.p. 62°–63°, b.p. 254°–255°/40 mm. *ac-Tetrahydro- β -naphthyl phenyl carbamate* crystallises in tufts of silky needles, m.p. 98.5°. *Sodium-ac-tetrahydro- β -naphthyl xanthate* is prepared readily by heating an ethereal solution of the sodium derivative of *ac-tetrahydro- β -naphthol* with carbon disulphide, and forms an ochre-yellow mass closely resembling sodium ethyl xanthate in properties; copper sulphate precipitates the brownish-black *cupric salt* from an aqueous solution, and this, like *eupric ethyl xanthate*, slowly changes to the ochre-yellow *cuprous salt* which crystallises from carbon disulphide in bright yellow crusts. The *phenyl urethane* derivative, pearly leaflets, m.p. 98°–99°, decomposes at 185°–200°, yielding carbon dioxide and pure Δ^1 -dihydronaphthalene (Bamberger and Lodter, *l.c.*; Straus and Rohrbacher, *l.c.*).

Tetrahydronaphthoic acids.—The behaviour of the naphthoic acids and their derivatives on reduction is of interest. β -Naphthoic acid either in ethyl alcoholic or amyl alcoholic solution is reduced by sodium in a normal manner to its alicyclic tetrahydro-derivative, whilst sodium- β -naphthoate on reduction in presence of nickel oxide under a hydrogen pressure of 119 atmospheres at a temperature of 360° for 50 hours yields a tetrahydro- β -naphthoic acid, m.p. 143°–144°, which, when this treatment is repeated, yields a mixture of decahydro- β -naphthoic acid and decahydronaphthalene. Sodium α -naphthoate, on the other hand, yields tetrahydronaphthalene under similar conditions to those employed for the hydrogenation of β -naphthoic acid (Ipatiew, Ber. 1909, 42, 2100). Moreover, 2-hydroxy- α -naphthoic acid, on treatment with sodium and ethyl alcohol yields a mixture of phenylene acetic propionic acid and *ac-* and *ar-tetrahydro- β -naphthols* (Einhorn and Lumsden, Annalen, 1895, 286, 257), whilst ethyl α -naphthoate yields methyl-1:4-dihydronaphthalene when treated in a similar manner, this methyldihydronaphthalene being formed also by a similar reduction of α -methylnaphthalene or α -naphthyl alcohol (de Pommereau, Compt. rend. 1921, 172, 1503).

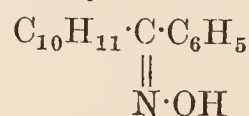
ar-Tetrahydro- α -naphthoic acid, slender prisms, m.p. 128° (Bamberger and Bordt), or 150° (von Braun), is obtained from *ar-tetrahydro- α -naphthylamine* by means of the diazo-reaction; *silver salt*, fine colourless needles; *copper salt*, light bluish-green precipitate; *lead salt*, glistening clusters of needles; *barium salt*, feathery needles; *amide*, flat satiny needles, m.p. 182° (Bamberger and Bordt, Ber. 1889, 22, 625; von Braun, etc., Ber. 1922, 55, 1700). A *carboxylic acid*, m.p. 161°–162°, *acetyl derivative*, m.p. 159°, has been obtained by F. Bayer & Co. (D. R. P. 335602, 1915), by heating a mixture of dry sodium *ar-tetrahydro- α -naphtholate* and carbon dioxide initially at 110° for 1 hour, and then at 210°.

ac-Tetrahydro- α -naphthoic acid is produced when *ac- Δ^2 -or Δ^1 -dihydro- α -naphthoic acid* is warmed with sodium amalgam in alkaline solution (Baeyer, Schoder and Besemfelder,

Annalen, 1891, 266, 169); when α -naphthoic acid is reduced with sodium and amyl alcohol (von Sowinski, Ber. 1891, 24, 2354); or in a yield of 95 p.c. by a similar reduction in absolute alcoholic solution using 5 times the theoretical quantity of sodium, followed by the purification of the crude product by oxidation with potassium permanganate to remove dihydro-compounds (Kay and Morton, Chem. Soc. Trans. 1914, 105, 1565).

ac-Tetrahydro- α -naphthoic acid crystallises in triclinic needles, m.p. 85° (Baeyer, &c.), or white needles, m.p. 80° (von Sowinski). The *silver* and *barium salts* are readily soluble and the free acid may be regenerated from the *ammonium salt* by evaporating the solution; *amide*, colourless needles, m.p. 116°; *ethyl ester*, b.p. 279°/747 mm. When *ac-tetrahydro- α -naphthoic acid* is treated with phosphorus pentachloride and then with bromine at 50°–60° it forms an extremely unstable *bromo acid*, which on pouring into absolute alcohol is converted into *ac-ethyl- α -bromotetrahydro- α -naphthoate*, a faintly yellow viscid oil, b.p. 208°/20 mm. with decomposition. This bromo-ester, on treatment with boiling diethyl-aniline, yields *ac-ethyl- Δ^1 -dihydro- α -naphthoate*, an oil, b.p. 300°–310°/756 mm., identical with that obtained by Rabe (Ber. 1898, 31, 1899). The latter ester on treatment with magnesium methyl iodide in ethereal solution forms *benzo- Δ^3 -nor-p-menthen-10-ol*, m.p. 101°–102°, with an odour resembling naphthalene. This product, on digesting with potassium pyrosulphate, loses water and is converted into *benzo- $\Delta^{3:10(11)}$ -nor-p-menthadiene*, b.p. 255°–256°/750 mm. The latter compound, on treatment with sodium in absolute alcoholic solution, at a temperature of 130° is reduced with difficulty, yielding *benzo- $\Delta^{10(4)}$ -nor-p-menthene*, b.p. 245°–247°/744 mm., which is identical with the isomerisation product of *benzo- $\Delta^{10(11)}$ -nor-p-menthene*. *ac-Ethyl-tetrahydro- α -naphthoate* when left in contact with an ethereal solution of magnesium methyl iodide is converted gradually into *benzo-nor-p-menthan-10-ol*, a viscous oil of camphoraceous odour, b.p. 166°/30 mm., which, on digestion with potassium pyrosulphate, is converted into *benzo- $\Delta^{10(11)}$ -nor-p-menthene*, b.p. 259°–261°/745 mm. The latter hydrocarbon, on treatment with 5 p.c. sodium ethoxide (*cf.* Straus and Lemmel, Ber. 1913, 46, 232) is partially isomerised into *benzo- $\Delta^{10(4)}$ -nor-p-menthene*. The above benzo-terpenes are of interest as being derivatives of tetrahydronaphthalene and forming a connecting link between naphthalene and the sesquiterpenes (Kay and Morton, Chem. Soc. Trans. 1914, 105, 1565). *Menthyl ac-tetrahydro- α -naphthoate* is a very viscous liquid, b.p. 207°/10 mm., $[\alpha]_D = -47.57^\circ$ (Rupe and Munter, Annalen, 1910, 373, 121).

ar-Tetrahydro- β -naphthoic acid, m.p. 152°–153°, b.p. 216°/14 mm., is formed by the action of oxalyl chloride on tetrahydronaphthalene (von Braun, Kirschbaum and Schuhmann, Ber. 1920, 53, 1161); by the hydrolysis of the anilide obtained by submitting the oxime,



to the Beekmann reaction (Scharwin, Ber. 1902, 35, 2511); and by the reduction of β -naphthoic

acid with hydrogen in presence of nickel oxide (Ipatiew, Ber. 1909, 42, 2100). On hydrogenation with sodium and amyl alcohol ar-tetrahydro- β -naphthoic acid is converted into *decahydro- β -naphthoic acid*, m.p. 79°, b.p. 190°–192°/21 mm. *ar-Tetrahydro- β -naphthoyl chloride*, an oil, b.p. 162°/13 mm., on treatment with ammonia yields the corresponding *amide*, shining leaflets, m.p. 137°–138°. The latter compound on treatment with bromine and alkali is converted into ar-tetrahydro- β -naphthylamine (von Braun, Kirschbaum and Schuhmann, l.c.).

ac-Tetrahydro- β -naphthoic acid is prepared by boiling ac-1:4-dihydro- β -naphthoic acid with sodium amalgam (von Sowinski, Ber. 1891, 24, 2354); by heating an alkaline solution of β -naphthoic acid with sodium amalgam until a test with permanganate shows the absence of oxidisable bodies (Baeyer, Schoder and Besm-felder, Annalen, 1891, 266, 169); and when β -naphthoic acid dissolved in a large quantity of amyl alcohol is boiled with sodium (von Sowinski, l.c.). *ac-Tetrahydro- β -naphthoic acid* forms transparent needles, m.p. 96° (Baeyer, &c.), or 94° (von Sowinski).

Menthyl ac-tetrahydro- β -naphthoate is a colourless viscid oil, b.p. 218°/11 mm., $[\alpha]_D^{20} = -53.04^\circ$ (benzene) (Rupe and Munter, Annalen, 1910, 373, 121).

1-Amino-5:6:7:8-tetrahydro-8-naphthoic acid, grey laminae, m.p. 150°–161° (decomp.), is obtained by reducing naphthastyril in sodium hydroxide solution with sodium amalgam; the *silver salt* forms the additive compound,



methyl ester, m.p. 53°–54°, *hydrochloride*, long needles. The free acid does not form a lactam even on prolonged boiling with hydrochloric acid.

Acetyltetrahydronaphthastyril, needles, m.p. 103°–104°, and 1-acetyl-amino-5:6:7:8-tetrahydro-8-naphthoic acid, m.p. 181°–182°, are both obtained by the action of acetic anhydride on the sodium salt of 1-amino-5:6:7:8-tetrahydro-8-naphthoic acid (Schroeter and Rössler, Ber. 1902, 35, 4222).

Tetrahydronaphthalene condenses with succinic anhydride forming *ar- β -2-tetrahydronaphthoyl-propionic acid*, m.p. 121°–122°; the derived *ar- γ -tetrahydronaphthyl-n-butyric acid*, colourless crystals, m.p. 49°–50°, when treated with concentrated sulphuric acid, yields 1-ketooctahydroanthracene, m.p. 46°–47°, b.p. 202°/13 mm., which forms a *semicarbazone*, m.p. 252°–253° (Krollpfeiffer and Schäfer, Ber. 1923, 56, 620).

ar-Tetrahydro- β -naphthoyl-o-benzoic acid, colourless needles, m.p. 153°–155°, is obtained by condensing tetrahydronaphthalene with phthalic anhydride in benzene solution in the presence of aluminium chloride. It forms a sparingly soluble *ammonium salt*; a *methyl ester*, m.p. 73°–74°; an *acetyl lactone*, colourless needles, m.p. 135°. On reduction with zinc amalgam and hydrochloric acid, it yields *ar-tetrahydro- β -naphthylmethyl-o-benzoic acid*, colourless crystals, m.p. 126°; *methyl ester*, colourless liquid, b.p. 234°–235°/15 mm. The latter is converted by hydrogen under pressure at 180°–200° in the presence of a nickel catalyst into

(?) *methyl ω -decahydro- β -naphthyl-o-toluate*, colourless viscous liquid, b.p. 222°/15 mm., which, on hydrolysis, is converted into a semi-solid *acid*, forming a *potassium salt* which possesses slight lathering properties. *Tetrahydronaphth-2:3-anthraquinone*, yellow needles, m.p. 211°, and *tetrahydronaphth-1:2-anthraquinone*, yellow needles, m.p. 135°, are formed by the action of fuming sulphuric acid on ar-tetrahydro- β -naphthoyl-o-benzoic acid. *ar-Tetrahydro- β -methyl-naphthalene*, colourless liquid, b.p. 220°–222°, obtained by the reduction of β -methyl-naphthalene with hydrogen in presence of a catalyst, condenses with phthalic anhydride in presence of aluminium chloride to give *ar-tetrahydro-3-methyl- β -naphthoyl-o-benzoic acid*, colourless needles, m.p. 160°. The latter, on treatment with fuming sulphuric acid, is converted exclusively into *tetrahydro-3-methyl-naphth-1:2-anthraquinone*, slender yellow needles, m.p. 119° (Schroeter, Ber. 1921, 54, 2242; Tetralin, G.m.b.H., D. R. P. 346673, 1918).

When α -methyl- β -naphthylamine is treated twice with sodium and amyl alcohol, *ar- α -methyl- β -amino-tetrahydronaphthalene*, colourless oil, b.p. 170°–175°/30 mm., is obtained; *acetyl-derivative*, leaflets, m.p. 134°; *benzoyl-derivative*, m.p. 222°; *hydrochloride*, colourless needles, m.p. 263°–264° (Mayer and Schnecko, Ber. 1923, 56, 1408).

The *ar-tetrahydro- β -methyl-naphthalene*, described above, is obtained also by reducing 7-methyl-ac-1-ketotetrahydronaphthalene with zinc amalgam and concentrated hydrochloric acid and has the following constants:—b.p. 224°–226°, d_4^{20} 0.950, n_D^{20} 1.535. *ar-Tetrahydro- β -ethyl-naphthalene*, b.p. 245°–246°, d_4^{20} 0.948, n_D^{20} 1.534, and *ar-tetrahydro-1:3-dimethyl-naphthalene*, colourless liquid, b.p. 250°–252°/atm., d_4^{20} 0.960, n_D^{20} 1.541, are produced also by the reduction of the corresponding ketones (Krollpfeiffer and Schäfer, Ber. 1923, 56, 620), whilst ar-tetrahydro- β -ethyl-naphthalene is produced also by reducing ar-tetrahydro-naphthyl- β -methylketone (Fleischer and Siefert, Ber. 1920, 53, 1255). ar-Tetrahydro- β -ethyl-naphthalene is decomposed when distilled in an atmosphere of carbon dioxide through a tube (empty or filled with pumice coated with lead oxide) at 650° forming β -ethyl-naphthalene, whereas at 700° the ethyl group is also eliminated with the formation of naphthalene (von Braun, Hahn and Seemann, Ber. 1922, 55, 1687).

The Friedel-Crafts reaction does not give rise to methyltetrahydronaphthalene, but tetrahydro-2-ethyl-naphthalene, b.p. 244°, is obtained in low yield. 2-iso-Propyltetrahydronaphthalene, b.p. 255°–256°, d_4^{16} 0.9518, is obtained similarly from *n*-propyl chloride and tetrahydronaphthalene; the formation of 2-tert-butyltetrahydronaphthalene, b.p. 265.5°–266.5°, d_4^{15} 0.9463, n_D^{15} 1.5348, is accompanied by evolution of isobutane; 2-tert-amyltetrahydronaphthalene, b.p. 149.2°–150°/12 mm., d_4^{17} 0.9478, n_D^{17} 1.5332 (Boedtker and Rambeeh, Bull. Soc. chim. 1924, [iv.] 35, 631).

1:6-Dimethyl- $\Delta^{6:7-5:8}$ -dihydronaphtha-

lene, b.p. 118°/10 mm., d^{16}_4 0.9700, is obtained by reducing 1 : 6-dimethylnaphthalene with sodium and amyl alcohol. On further reduction with hydrogen in aqueous alcoholic solution in presence of palladium, 1 : 6-dimethyl-5 : 6 : 7 : 8-tetrahydronaphthalene, colourless liquid, b.p. 110°–111°/11 mm., d^{16}_4 0.9487, is obtained. The latter product is oxidised by nitric acid to benzene 1 : 2 : 3-tricarboxylic acid. When the reduction of 1 : 6-dimethylnaphthalene is carried out at 240° under 20–25 atmospheres pressure in the presence of a nickel catalyst, a mixture (b.p. 108°–110°/10 mm., d^{16}_4 0.9504) of 1 : 6-dimethyl-1 : 2 : 3 : 4-tetrahydronaphthalene and 1 : 6-dimethyl-5 : 6 : 7 : 8-tetrahydronaphthalene is obtained, which is oxidised by nitric acid to a mixture of benzene 1 : 2 : 3- and 1 : 2 : 4-tricarboxylic acids (Mayer and Schulte, Ber. 1922, 55, 2164).

2 : 6-Dimethyl- $\Delta^{2:3}$ -dihydronaphthalene, b.p. 125°–126°/15 mm., is obtained by the reduction of 2 : 6-dimethylnaphthalene with sodium and amyl alcohol. It forms a liquid *dibromide*, which on distillation is decomposed into hydrobromic acid and 2 : 6-dimethylnaphthalene (Mayer and Alken, Ber. 1922, 55, 2278).

ar-Tetrahydro- α -naphthaldehyde, colourless, almost odourless liquid, b.p. 131°–133°/12 mm. (von Braun, etc., Ber. 1922, 55, 1700), or 130°–140° (mainly 135°)/18 mm. (Fleischer and Feldmeier, Ber. 1922, 55, 3290), is obtained from ar-tetrahydro- α -methylnaphthalene by Etard's reaction (Fleischer and Feldmeier), or by the oxidation of *ar-tetrahydro- α -naphthylalcohol*, b.p. 154°–155°/12 mm., with potassium dichromate and sulphuric acid (von Braun, etc.). It forms a *semicarbazone*, m.p. 187°, and a *bisulphite compound*. The *alcohol*, b.p. 154°–155°/12 mm., is obtained by the action of sodium nitrite and acetic acid on ar-tetrahydro- α -naphthylmethylamine (von Braun, etc.).

ar-Tetrahydro- α -naphthaldehyde, colourless mobile liquid with a peppermint odour, b.p. 150°–155°/14 mm. (Fleischer and Feldmeier) or 138°/14 mm. (von Braun, etc.), yields a *semicarbazone*, m.p. 219° (von Braun, etc.) or 221°–223° (Fleischer and Feldmeier), and a *bisulphite compound*, whilst the *oxime* shows little tendency to crystallise. The aldehyde is formed in a similar manner to the α -isomeride, either from ar-tetrahydro- β -methylnaphthalene (Fleischer and Feldmeier, Ber. 1922, 55, 3290) or from the corresponding *alcohol*, pale yellow liquid with a powerful pleasant odour, b.p. 148°–152°/14 mm., or, in small yield, from tetrahydronaphthalene by the action of carbon monoxide, hydrogen chloride and aluminium chloride (von Braun, etc., Ber. 1922, 55, 1700).

ac-Tetrahydro- β -naphthaldehyde, oil, b.p. 122°/12 mm., is formed by the reduction of β -naphthol 3-carboxylic acid, 2-acetoxy-naphthalene 3-carboxylic acid, 1-amino- β -naphthol 3-carboxylic acid, or 1-bromo- β -naphthol 3-carboxylic acid, by means of sodium amalgam in presence of boric acid, with the addition of a neutral mixture of sodium sulphite and sodium hydrogen sulphite; ammonia and hydrogen bromide, respectively, are eliminated from the last two naphthol derivatives. The *bisulphite compound* is freely soluble in water. *ac-Tetrahydronaphthalene- β -phenylhydrazone* crystallises from alcohol containing a little

glacial acetic acid, m.p. 106.5° (Weil and Oestermeier, Ber. 1921, 54, 3219; Weil and Hcerdt, *ibid.* 1922, 55, 224).

Hydrogenated naphthalene dicarboxylic acids.—Naphthalic anhydride can be hydrogenated when platinum is used as catalyst, only if the latter is activated from time to time by oxygen. The reaction products include the tetra- and decahydro-anhydrides, decahydroacenaphthene, and *tetrahydro-1-methylnaphthalene 8-carboxylic acid*, needles, m.p. 150°. Naphthalic acid, containing traces of anhydride, also can only be hydrogenated in a similar manner, whereas, pure naphthalic acid can be hydrogenated under the ordinary conditions with platinum to form tetrahydronaphthalic acid (Willstätter and Jaquet, Ber. 1918, 51, 767, 774).

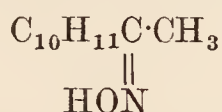
Casares and Ranedo (Anal. Fis. Quim. 1922, 20, 519), on the other hand, state that naphthalic acid, when reduced with hydrogen in presence of platinum, yields *decahydronaphthalic acid* (probably a mixture of *cis*- and *trans*-isomerides) which has no definite melting-point, and that the methyl and ethyl esters are more readily hydrogenated than the parent acid.

Tetrahydronaphthalene 1 : 8-dicarboxylic acid, obtained as above, or by heating a mixture of dihydronaphthalic acid, red phosphorus and hydriodic acid (b.p. 127°) for 5 hours at 140°–145° (Zengelis, Ber. 1894, 27, 2694) crystallises in prisms, m.p. 196°, and on heating is converted into the *anhydride*, m.p. 119.5°. The latter does not form an imide, and thus resembles the dihydro-derivative in this respect. On treatment with hydrochloric acid and ethyl alcohol at lower temperatures, tetrahydronaphthalic acid yields the *acid ester*, colourless crystals, m.p. 48°, whilst at higher temperatures mainly the anhydride is formed. Casares and Ranedo (*l.c.*) have obtained the following compounds: *methyl tetrahydronaphthalene 1 : 8-dicarboxylate*, crystals, m.p. 74°; *ethyl tetrahydronaphthalene 1 : 8-dicarboxylate*, crystals, m.p. 52°; *methyl decahydronaphthalene 1 : 8-dicarboxylate*, crystals, m.p. 103°–105°. Moro (Gazz. chim. ital. 1896, 26, i. 89) by reducing naphthalene-1 : 5-dicarboxylic acid with sodium amalgam obtained *tetrahydronaphthalene-1 : 5-dicarboxylic acid*, needles, m.p. 237.5°–238.5°; *calcium salt* + $3\frac{1}{2}\text{H}_2\text{O}$; *barium salt* + H_2O , nearly white laminæ; whilst the *ethyl and methyl ester* are liquids.

ac-Tetrahydronaphthalene 2 : 3-dicarboxylic acid, m.p. 199°, with formation of the anhydride, is obtained in the following manner. Ethylsodiummonochloro-malonate is condensed with *o*-xylylene dibromide, and the product is converted into the sodium derivative of ethyl-*o*-xylyl dimalonate by digestion with zinc dust and acetic acid. The latter compound, on treatment with an ethereal solution of iodine, yields ethyl-*ac-tetrahydronaphthalene tetracarboxylate*, from which two molecules of carbon dioxide are eliminated during hydrolysis with formation of *ac-tetrahydronaphthalene 2 : 3-dicarboxylic acid*; also formed by the action of *o*-xylylene dibromide on ethyl-di-sodium acetylene tetracarboxylate. The *silver salt* of *ac-tetrahydronaphthalene 2 : 3-dicarboxylic acid* decomposes when heated, forming its *anhydride*, m.p. 184°, and some naphthalene also is formed (Baeyer and Perkin, Ber. 1884,

17, 448; Perkin, Chem. Soc. Trans. 1888, 53, 11, 20; Proc. Chem. Soc. 1887, 3, 93).

ar-Tetrahydro-β-naphthyl methyl ketone, a colourless aromatic liquid, b.p. 182°/20 mm., which turns yellow on keeping, is produced by the action of acetyl chloride on tetrahydronaphthalene in carbon disulphide solution in presence of aluminium chloride. The energetic reaction, and the difficulty of obtaining a pure product, is probably due to the presence of dihydronaphthalene as an impurity, for pure tetrahydronaphthalene reacts slowly on similar treatment; *semicarbazone*, m.p. 234°–235°. The only *oxime*, colourless needles, m.p. 106°, obtained from this ketone has the configuration



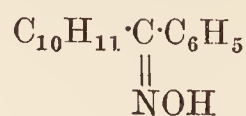
When this oxime is submitted to the Beckmann reaction, *ar-tetrahydroaceto-β-naphthalide*, small colourless needles, m.p. 107°, is formed and, on hydrolysis with boiling 45 p.e. sulphuric acid, yields *ar-tetrahydro-β-naphthylamine*. *ar-Tetrahydro-β-naphthyl methyl ketone*, when distilled in an atmosphere of carbon dioxide through a tube (empty or filled with pumice coated with lead oxide) at 680°–700°, is converted into *β-naphthylmethylketone* (von Braun, Hahn and Seemann, Ber. 1922, 55, 1687).

ar-Tetrahydro-β-naphthyl methyl ketone condenses with isatin in boiling aqueous, alcoholic, alkaline solution forming *2-β-tetrahydronaphthyl-cinchoninic acid*, m.p. 198°–199° (decomp.); *ethyl ester*, needles, m.p. 86°. When heated until the evolution of carbon dioxide ceases, the acid is converted into *2-β-tetrahydronaphthylquinoline*, needles, m.p. 75°. With 6-bromoisatin the methyl ketone yields the corresponding *bromo-derivative*, yellow crystals, m.p. 228°–229.5° (von Braun, Hahn and Seemann, *l.c.*; Chem. Fabrik, vorm. E. Schering, H. Emde and E. Freund, D. R. P. 344027, 1920).

ar-Tetrahydro-β-naphthyl methyl ketone, when heated with dimethylamine hydrochloride and powdered paraform in absolute alcoholic solution, yields the *hydrochloride* of *β-tetrahydronaphthyl-β-dimethylaminoethyl ketone*, needles, m.p. 170°. The *base* is an oil which forms a *picrate*, needles, m.p. 156°. The hydrochloride, when reduced with hydrogen in presence of platinum-black, yields the *hydrochloride* of *β-tetrahydronaphthyl-ω-dimethylaminoethyl carbinol*, leaflets, m.p. 163°. The free *base* is a colourless liquid. The methyl ketone, when treated with piperidine hydrochloride and paraform in a similar manner, yields the *hydrochloride* of *β-piperidinoethyl-β-tetrahydronaphthyl ketone*, m.p. 170° (anhydrous) or 85° (+aq.). The free *base* is a viscous liquid which forms a *nitrate*, needles, m.p. 134°–135°, and an *oxime hydrochloride*, silky needles, m.p. 211° (Mannich and Lammering, Ber. 1922, 55, 3510). *ar-Tetrahydro-β-naphthyl phenyl ketone*, viscous yellow oil, b.p. 222°–223°/12 mm., is prepared in a similar manner by the use of benzoyl chloride. It forms an oxime which can be separated by fractional crystallisation from acetic acid and alcohol into the less soluble *oxime*, white needles, m.p. 142°



and its *stereoisomeride*, white needles, m.p. 116°,



The former is converted in the usual manner into the *benzoyl derivative* of *ar-tetrahydro-β-naphthylamine*, colourless needles, m.p. 166°–167°, whilst the latter yields the *anilide* of *ar-tetrahydro-β-naphthoic acid*, m.p. about 141°, which on hydrolysis, yields *ar-tetrahydro-β-naphthoic acid*, m.p. 153° (Scharwin, Ber. 1902, 35, 2511; Hesse, Ber. 1920, 53, 1645). *ar-Tetrahydro-β-naphthyl methyl ketone* is reduced to *ar-2-ethyltetrahydronaphthalene*, b.p. 127°/21 mm., which, on regulated acetylation and reduction, yields successively *ar-2:3-diethyltetrahydronaphthalene*, b.p. 150°–151°/18 mm., and *ar-1:2:3-triethyltetrahydronaphthalene*, b.p. 165°–172°/23 mm.

Tetrahydronaphthalene reacts with ethylacetyl chloride in presence of phosphoric oxide forming *α-* and *β-tetrahydronaphthoylacetyl chlorides*, which, on treatment with ethyl sodiomalonate, yield *ethyl α-* and *β-tetrahydronaphthoylacetyl malonates*. These latter, on hydrolysis, yield *α-* and *β-tetrahydronaphthoylpropionic acids*, which on reduction give rise to *α-* and *β-tetrahydronaphthylbutyric acids*. The chlorides of these acids yield cyclic ketones by inner condensation. *β-Tetrahydronaphthylbutyryl chloride* yields *4-keto-s-octahydroanthracene* and *4-keto-s-octahydrophenanthrene*. The former, on reduction, gives rise to *s-octahydroanthracene*, m.p. 72°–73°, identical with that prepared by direct catalytic reduction (Schroeter and Tetralin, G.m.b.H., D. R. P. 352721, 1920).

Tetrahydronaphthalene and dimethylmalonyl chloride yield exclusively *2:2-dimethyl-ar-tetrahydronaphth-αβ-indane-1:3-dione*, m.p. 75°, which on hydrolysis yields *1-isobutyryl-ar-tetrahydronaphthalene 2-carboxylic acid*, m.p. 120°. The indanedione is reduced by amalgamated zinc and hydrochloric acid to *2:2-dimethyl-ar-tetrahydronaphth-αβ-hydrindene*, b.p. 156°/18 mm., which reacts with dimethylmalonyl chloride, to give *2:2:5:5-tetramethyl-ar-tetrahydronaphth-dihydrindene-4:6-dione*, m.p. 148°–149°. The latter on reduction yields the corresponding *dihydrindene*, m.p. 105°–106°. Contrary to the statement of von Braun, Kirsebaum and Schuhmann, tetrahydronaphthalene with diethylmalonyl chloride yields both isomerides, *2:2-diethyl-ar-tetrahydronaphth-ββ-indane-1:3-dione*, m.p. 118°, and *2:2-diethyl-ar-tetrahydronaphth-αβ-indane-1:3-dione*, m.p. 54°–55° (Fleischer and Siefert, Ber. 1920, 53, 1255), or 56°–57°, b.p. 207°–211°/15 mm. (von Braun, &c.); only the latter yields a well-defined *acid*, m.p. 135°. These diones are reduced completely by amalgamated zinc and hydrochloric acid into the respective hydrocarbons, *2:2-diethyl-ar-tetrahydronaphth-ββ-hydrindene*, m.p. 49°; *2:2-diethyl-ar-tetrahydronaphth-αβ-hydrindene*, b.p. 163°–165°/12 mm. By continued reduction of the latter the hydrindene ring is ruptured with the formation of *γ-methyl-γ-ethylbutyl-ar-tetrahydronaphthalene*, b.p. 141°–144°/11 mm. (von Braun, Kirschbaum and Schuhmann, Ber. 1920, 53, 1161; Fleischer and Siefert, *ibid.* 1255).

2-Ethyl-ar-tetrahydronaphthalene, when con-

densed with diethylmalonyl chloride in presence of aluminium chloride and carbon disulphide, forms 2:2:4-triethyltetrahydronaphth- $\alpha\beta$ -indane-1:3-dione, colourless crystals, m.p. 39° (Fleischer and Retze, Ber. 1923, 56, 228).

Tetrahydrodinaphthylene- α -oxide, colourless needles, with a faint blue fluorescence, m.p. 128°, is obtained by reducing α -dinaphthylene oxide, m.p. 178°–179°, with sodium and amyl alcohol. Treatment with bromine in chloroform solution yields a *dibromo-substituted derivative*, glistening leaflets, m.p. 251°, unaffected by alcoholic potassium hydroxide or silver nitrate (Hönigschmid, Monatsh. 1901, 22, 561; 1902, 23, 829).

ac-1-Keto-3-methyltetrahydronaphthyl-3-acetic acid, stellate clusters of colourless prisms, m.p. 155°–156°, is obtained by hydrolysing the imide, derived by Guareschi's process (Atti R. Accad. Sci. Torino, 1900–1901, 36, 443) from benzyl methyl ketone, with a large excess of 50 p.c. (by volume) sulphuric acid; *semicarbazone*, fine needles, m.p. 221°; *ac-1-keto-3-ethyltetrahydronaphthyl-3-acetic acid*, short stout prisms, m.p. 79°; *semicarbazone*, needles, m.p. 210°; *1-keto-3-methyloctahydronaphthyl-3-acetic acid*, colourless crystals, m.p. 90°; *semicarbazone*, spherical aggregates of needles, m.p. 209°–210° (decomp.) (Kon and Stevenson, Chem. Soc. Trans. 1921, 119, 87).

Colouring matters derived from tetrahydronaphthalene derivatives.—The manufacture of tetralin on the large scale, coupled with the fact that it can be submitted to the usual reactions for the production of intermediate products from hydrocarbons, such as nitration, amidation, sulphonation, hydroxylation, &c., will undoubtedly place a large new series of intermediate products at the disposal of the colour manufacturer. The literature contains numerous references to colouring matters, mainly azo-dyes, described by various workers, but the fastness and other properties of such products have only been investigated recently (Rowe and Tarbett, J. Soc. Dyers, 41, 1925, 5). In this connection it would appear that the aromatic amino-derivatives may prove useful intermediates for the production of azo-dyes. The aromatic tetrahydronaphthylamines have been shown to possess many interesting peculiarities. Bamberger and Bordt (Ber. 1889, 22, 625) stated that ar-tetrahydro- β -naphthylamine may be coupled with diazonium salts with the formation of azo-derivatives, but this was shown to be incorrect by Smith (Chem. Soc. Trans. 1902, 81, 900), who found that ar-tetrahydro- β -naphthylamine forms intermediate diazoamines, but does not form amino-azo compounds. In this case the naphthalenoid properties have, therefore, disappeared completely as a result of hydrogenation, and the behaviour is in all respects that of a benzenoid amine. On the other hand, ar-tetrahydro- α -naphthylamine retains the naphthalenoid characteristic of reacting with diazonium salts under ordinary conditions to form amino-azo compounds without the intermediate formation of diazoamines. In all other respects, ar-tetrahydro- α -naphthylamine resembles a benzenoid amine. Derivatives of ar-tetrahydro- α -naphthylamine containing a bromine atom, or a sulphonic group in the 4-position, however, do form diazoamino compounds, which undergo the characteristic fission with

concentrated hydrochloric acid, without formation of azo-colouring matters. This led Morgan, Micklethwait and Winfield (Chem. Soc. Trans. 1904, 85, 743) to the conclusion that as regards this condensation, the reactivity of a hydrogen atom in the α -position adjacent to the amino-group is a characteristic feature of the naphthalene molecule which is destroyed when the non-substituted ring undergoes hydrogenation. Of further interest is the fact that azo-dyes derived from ar-tetrahydro- α -naphthylamine and its derivatives differ considerably in shade from azo-dyes of similar constitution derived from α -naphthylamine and its derivatives, approximating in this respect to dyes derived from a xylidine.

Diazoamines of ar-tetrahydro- β -naphthylamine have the general appearance of benzenoid diazoamines, and are obtained either by the action of a benzene diazonium salt on the tetrahydro-base or by coupling benzenoid amines with an ar-tetrahydro- β -naphthalene diazonium salt.

p-Toluenediazoaminotetrahydro- β -naphthalene, straw-coloured flakes, m.p. 107°. A similar diazoamine is formed when *p*-toluidine is replaced by *o*-toluidine.

p-Nitrobenzenediazoaminotetrahydro- β -naphthalene, chocolate-brown prisms, m.p. 179° with violent decomposition, is obtained from diazotised *p*-nitroaniline and the tetrahydro-base, but cannot be obtained by using diazotised ar-tetrahydro- β -naphthylamine and *p*-nitroaniline in aqueous, alcoholic or glacial acetic acid solution.

o-Nitrobenzenediazoaminotetrahydro- β -naphthalene, yellow plates, m.p. 134°, is prepared from *o*-nitrobenzene diazonium chloride, but cannot be obtained from the diazotised tetrahydro-base. The *m*-isomeride decomposes at 0° into a dark-red viscid liquid. *p-Bromobenzenediazoaminotetrahydro- β -naphthalene*, primrose-yellow silky needles, m.p. 134°; the *m-chloro-analogue* rapidly changes into a viscid red oil; *β -naphthalenediazoaminotetrahydro- β -naphthalene*, lustrous yellow plates, m.p. 137·5°, is formed when diazotised β -naphthylamine is condensed with the tetrahydro-base, whilst if the tetrahydro-base be diazotised and coupled with β -naphthylamine, *tetrahydro- β -naphthalene-azo- β -naphthylamine*, dark red tables, m.p. 130°, is obtained; *tetrahydronaphthalene-4-diazo-amino- β -tetrahydronaphthalene*, amber-coloured prisms, m.p. 104° (Smith, Chem. Soc. Trans. 1902, 81, 900). *4-Bromotetrahydronaphthalene- α -diazoamino-4-bromo- α -tetrahydronaphthalene*, orange-yellow needles, decomposing violently at 190°–194°, cannot be converted into the isomeric aminoazo compound by digestion at 70° with a mixture of the bromo-base and its hydrochloride (cf. Noelting and Witt, Ber. 1884, 17, 78; Smith, Chem. Soc. Trans. 1902, 8, 900).

p-Nitrobenzenediazoamino-4-bromo- α -tetrahydronaphthalene, brownish-yellow leaflets, m.p. 178°, with violent decomposition; *o-nitrobenzenediazoamino-4-bromo- α -tetrahydronaphthalene*, orange-brown needles, m.p. 170°–175°, with violent decomposition; *m-nitrobenzenediazoamino-4-bromo- α -tetrahydronaphthalene*, orange-brown prisms, m.p. 165°–166°, with violent decomposition; *coumarin-6-diazoamino-4-bromo- α -tetrahydronaphthalene*, brownish-yellow nodular

crystals, m.p. 165°–168° (decomp.) (Morgan, Micklethwait and Winfield, *l.c.*). *ac*-Tetrahydro- β -naphthylamine in its behaviour towards benzene diazonium chloride resembles the non-aromatic amines, such as dimethylamine or ethylamine, and yields a *diazoamino-derivative*, which is weakly basic and volatile with steam. It is explosive, and, when heated with dilute acids, is decomposed for the most part into dihydronaphthalene and aniline with evolution of nitrogen. It forms a *picrate*, m.p. 118° (Bamberger and Müller, *Ber.* 1888, 21, 1112). *Benzene-4-azo-tetrahydro- α -naphthylamine*, steel-blue needles of vitreous lustre, dissolves in alcohol and ether with a dark bordeaux-red colour. *Sodium-p-sulphobenzene-4-azo-ar-tetrahydro- α -naphthylamine*, orange-red tables, dyes wool orange from an acid bath. *ar-Tetrahydro-naphthalene- α -azo- α -naphthylamine*, brick-red silky needles, m.p. 135°, and a second *product*, small green cubes, dissolving in acetic acid with a violet colour, is produced also during its preparation.

Tetrahydronaphthalene- α -azo-resorcinol, slender brick-red scales, m.p. 219° (decomp.) (Bamberger and Bordt, *Ber.* 1889, 22, 625). *5-Aminotetrahydronaphthalene- α -azo- β -naphthylamine*, orange-red prisms with a metallic lustre, m.p. 282° with violent decomposition (Bamberger and Bammann, *Ber.* 1889, 22, 951); *p-sulphobenzene-4-azo-tetrahydro-5-aminotetrahydro- α -naphthol*, lustrous lemon-coloured rosettes. The *sodium salt* dissolves in water with a dark bordeaux-red colour, and the *hydrochloride* with a carmine colour (Bamberger and Bammann, *l.c.*). *ar-Tetrahydroethyl- α -naphthylamine* couples with diazobenzene-*p*-sulphonic acid to form an orange-red dye, whilst the corresponding dimethyl derivative yields a dye, the *sodium salt* of which crystallises in yellow plates (Bamberger and Helwig, *Ber.* 1889, 22, 1311).

Benzene-azo-ar-tetrahydro- α -naphthol, cantharides-green tablets of metallic lustre, m.p. 144°–145°, the green crystals begin to lose their metallic lustre at 110° and become orange-red at 120°; *bis-benzene-azo-tetrahydro- α -naphthol*, m.p. 156° (Jacobson and Turnbull, *Ber.* 1898, 31, 890); *p-sulphobenzene-4-azo-tetrahydro- α -naphthol*, scarlet-red flocks, *sodium salt*, orange-red scales with a bronzy lustre (Bamberger and Bordt, *Ber.* 1890, 23, 215); *p-sulphobenzene-1-azo-tetrahydro- β -naphthol* is bordeaux-red in colour (Bamberger and Kitschelt, *Ber.* 1890, 23, 885); *tetrahydronaphthalene- β -azo- β -naphthol*, vermilion-red crystals with a green reflex, m.p. 153° (Smith, *Chem. Soc. Trans.* 1902, 81, 900).

ar-Tetrahydro- α -naphthylamine 8-carboxylic acid when diazotised and coupled with β -naphthol gives a red dye (Schroeter and Rössler, *Ber.* 1902, 35, 4222).

Naphthalene- α -azo-tetrahydro- α -naphthylamine, reddish-black nodular crystals; *p-nitrobenzene- α -azo-tetrahydro- α -naphthylamine*, dark brown flakes; *tetrahydronaphthalene- α -azo-tetrahydro- α -naphthylamine*, orange-brown needles, m.p. 135°–140°. *Ditolyl-disazo-bis-tetrahydro- α -naphthylamine* is a black powder which when tetrazotised and coupled with 1:8-dihydroxynaphthalene 3:6-disulphonic acid or with α -naphthol 4-sulphonic acid forms black powders with a metallic lustre, which dissolve in water with

a violet colour, and in concentrated sulphuric acid with an intense blue colour. The former dyes greyish-blue shades on unmordanted cotton and the latter heliotrope shades. The monoazo compound obtained by coupling *ar-tetrahydro- α -naphthylamine* with tetrazotised tolidine, when again diazotised and coupled with 1:8-dihydroxynaphthalene 3:6-disulphonic acid or with α -naphthol 4-sulphonic acid forms products which dye unmordanted cotton dark blue and reddish-heliotrope shades, respectively. *p-Nitrobenzene-4-azo-tetrahydrodimethyl- α -naphthylamine* forms deep red acicular prisms, m.p. 150°–152°; *sodium-p-sulphobenzene-4-azo-tetrahydrodimethyl- α -naphthylamine*, reddish-brown flakes which dye wool a red shade from an acid bath (Morgan and Richards, *J. Soc. Chem. Ind.* 1905, 24, 652).

Tetrahydro- β -naphthol 3-sulphonic acid forms strongly coloured azo-dyes when coupled with diazonium salts; *p-nitrobenzene-1-azo-tetrahydro- β -naphthol 3-sulphonic acid*, dark red crystals; *p-sulphobenzene-1-azo-tetrahydro- β -naphthol 3-sulphonic acid* dyes wool orange-brown shades from an acid bath; *4-sulpho-naphthalene-1-azo-tetrahydro- β -naphthol 3-sulphonic acid* dyes wool reddish-brown shades from an acid bath (Schroeter, &c., *Annalen*, 1922, 426, 123).

4-Acetylaminotetrahydronaphthalene- α -azo- β -naphthol 3:6-disulphonic acid dyes reddish-brown shades on wool as compared with the brownish-red shades obtained with the corresponding dye derived from monoacetyl-*p*-phenylenediamine (Azo Corallin L). Cotton padded with alkaline β -naphthol, dried and passed through a bath of diazotised 4-nitro-*ar-tetrahydro- α -naphthylamine* is coloured bright red as compared with the scarlet colour of Para Red, and with the red-brown shade similarly obtained with diazotised 4-nitro- α -naphthylamine. *4-Nitrotetrahydronaphthalene- α -azo-salicylic acid*, yellowish-brown powder, dyes chrome mordanted wool an orange-brown shade as compared with the reddish-yellow shade similarly obtained with *p-nitrobenzene-azo-salicylic acid* (Alizarin Orange R), and with the deep brown shade similarly produced with 4-nitronaphthalene- α -azo-salicylic acid (Rowe, *J. Soc. Dyers*, 1919, 35, 128).

The isomeric dihydro- α -naphthylamines are interesting on account of the fact that they form azo-dyes which differ considerably in shade from similar azo-dyes derived from α -naphthylamine or *ar-tetrahydro- α -naphthylamine*. The relation of the shades produced is well shown by the following examples: *Tetrahydronaphthalene- α -azo- β -naphthol* produces vivid orange-red shades; *5:8-dihydronaphthalene- α -azo- β -naphthol* yields a red, rather bluer than Para Red; *7:8- or 5:6-dihydronaphthalene- α -azo- β -naphthol* is orange-red, whilst *naphthalene- α -azo- β -naphthol* is a claret-red.

F. Bayer & Co. (D. R. P. 301671, 1915) have indicated the use of *ar-tetrahydro- α -naphthylamine* for the production of azo-dyes on the fibre. Cotton padded with an alkaline solution of the *ar-tetrahydro- α -naphthalide* of 2:3-dihydroxynaphthoic acid, m.p. 183°–184°, is treated with unsulphonated diazo-compounds. In this manner red shades are obtained from *p-nitroaniline*, scarlet from 4-nitro-2-anisidine, and blue from

dianisidine. The shades in all cases are stated to be fast to chlorine and boiling. The use of tetrahydronaphthalene derivatives has been suggested for the production of sulphide dyes. Thus, the indophenol or leuco-indophenol derived from *p*-aminophenol and ar-tetrahydro- α -naphthylamine on thionation forms a sulphide colour dyeing unmordanted cotton fast blue shades from a sodium sulphide or hydrosulphite bath (Buff and Thauss, U.S. Pat. 1175230, 1916; cf. Bayer & Co. Brit. Pat. 13952, 1915; D. R. P. 338817).

2-Tetrahydronaphthalene-2'-indoleindigotin, obtained by the condensation of ac-1-ketotetrahydronaphthalene and α -isatinanil, dyes wool and cotton blue shades from a yellow alkaline hydrosulphite vat; whilst 1-keto-2:3'-oxy-2'-thionaphthentetrahydronaphthalene, obtained by condensing the ketone with α -thionaphthenquinoneanil, dyes wool dark brownish-violet shades and cotton reddish-violet shades from a greenish-yellow alkaline hydrosulphite vat (Herzog and Kreidl, Ber. 1922, 55, 3394).

The physiological action of hydrogenated naphthalene derivatives.—Pohl and Rawicz (Zeitsch. physiol. Chem. 1919, 104, 95) showed that tetrahydronaphthalene possesses slightly toxic properties. They found that 2–3 grms. can be administered to rabbits (2 kilos.) without any apparent symptoms, whilst smaller animals develop diarrhoea and die, exhibiting narcosis.

Tetrahydronaphthalene administered to the rabbit is excreted as ac-tetrahydro- α -naphthalene-glycuronic acid, colourless lustrous plates, m.p. 256°–258°.

Röckemann (Arch. expt. Path. Pharm. 1922, 92, 52), however, isolated a dextro-rotatory compound, $C_{10}H_{12}O$, probably ac-tetrahydro- β -naphthol from the urine of rabbits fed with tetrahydronaphthalene.

When tetralin is administered to man, 5–7 grms. per day, the urine is inactive, dark green and readily yields an amorphous pigment. It also contains a leuco-compound besides dihydronaphthalene and naphthalene. The dihydronaphthalene is chiefly excreted as the conjugated glycuronic acid, which readily yields naphthalene. Other substances isolated from the urine, such as ac-tetrahydro- α -naphthyl carbamide, and a substance, m.p. 286°, are regarded as products of secondary reactions. Schroeter and Thomas (Zeitsch. physiol. Chem. 1918, 101, 262), on the other hand, showed that tetralin in its passage through the body of a dog is converted into *dl*-ac-tetrahydro- α -naphthyl-carbamide, whereas Röckemann (*l.c.*) states that only dihydronaphthalene could be isolated from the urine. He regards the formation of this hydrocarbon as being due to the loss of water from ac-tetrahydro- α -naphthol, which is assumed to be an earlier metabolic product.

Schroeter (Annalen, 1922, 426, 93) found that ar-tetrahydro- β -naphthol, its 1-bromo- and 1:3-dibromo-derivatives possess bactericidal properties, and have been used in the cases of *B. Coli*, *Staphylococcus pyog. alb.* and *Anthrax* spores.

Bamberger and Müller (Ber. 1888, 21, 1124) first drew attention to the mydriatic properties of ac-tetrahydro- β -naphthylamine, whilst Bamberger and Filehne (*ibid.* 1889, 22, 777) investi-

gated its action more closely. In extending the investigation, they showed that the physiological activity of ac-tetrahydro- β -naphthylamine was shared by its alkylated derivatives, for example, its ethyl and dimethyl derivatives. These authors concluded that the alicyclic hydrogenated bases of the β -series possessed mydriatic properties, whilst other members (aromatic) of the series of hydrogenated amines were inactive as far as mydriasis was concerned, and further stated that the activity of these alicyclic hydrogenated compounds was connected with the grouping $C \begin{smallmatrix} H \\ \diagup \\ NH_2 \end{smallmatrix}$ in the β -position. That

physiological activity is not the characteristic of all alicyclic hydrogenated β -naphthylamine derivatives is shown by the work of Leroux (Ann. Chim. 1910, [8] 21, 536), who found that decahydro- β -naphthylamine is devoid of mydriatic properties.

Cloetta and Waser (Arch. expt. Path. Pharm. 1913, 73, 398) and Waser (Schweiz. Chem. Zeit. 1917, 1, 12) have studied the physiological action of ac-tetrahydro- β -naphthylamine and its salts. They conclude that there is no appreciable difference in the physiological activity of the tetrahydro-base and its optically active modifications, and no relation has been found to exist between the dissociation capacities of the various salts examined and their toxicity. The monomethyl derivative, like the parent base, dilates the pupil and produces high fever; the monoethyl compound acts in the same way, but is more toxic. The introduction of acyl groups produces a diminution in the physiological activity. Whereas the acetyl derivative is more poisonous to frogs, the reverse is the case with warm blooded creatures (dogs), in which a contraction of the pupil, and a lowering of the temperature and blood pressure is observed. These properties are in strong contrast to the action of the base itself. A similar behaviour is shown by the CHO , COC_6H_5 , $CO_2C_2H_5$, $CONHC_6H_5$, $CSNHC_6H_5$, and $CSNHC_2H_5$ derivatives. *N*-Acyl-*N*-alkyl derivatives produce effects which are a combination of those of the monosubstituted derivatives. Thus, injection of *N*-acetyl- (or formyl) *N*-methyl-ac-tetrahydro- β -naphthylamine produces, on the one hand, dilation of the pupil (effect of the methyl derivative) and, on the other, a lowering of the temperature (Cloetta and Waser, *l.c.*; cf. Stein, Virchow's Archiv. für pathologische Anatomie und Physiologie, 1889, 115, 14; Fawcett and White, J. Physiol. 1897, 21, 435; Sacharoff, Zeitsch. expt. Path. Ther. 1909, 7, 224; Mutch and Pembrey, J. Physiol. 1911, 43, 109; Black, Proc. Roy. Soc. Edin. 1911, 31, 333).

The resolution and optical properties of hydrogenated naphthalene derivatives.—Bamberger (Ber. 1890, 23, 291) resolved ac-ar-tetrahydro-1:5-naphthylenediamine into its optically active components. An aqueous solution of the hydrogen tartrates of the optically inactive base is concentrated to a syrup, and a trace of conine dextrotartrate is added. Slender needles of the *l*-rotatory modification separate; hydrochloride, transparent lustrous prisms, in aqueous solution $[\alpha]_D = -7^\circ 29' 50''$. The *d*-rotatory modification separates from the mother-liquors of the isomeride after keeping in lustrous

needles; *hydrochloride* in aqueous solution $[\alpha]_D = +8^\circ 8' 49''$.

The resolution of *ac-tetrahydro- β -naphthylamine* into its optically active components has been effected by means of ammonium bromo-camphor sulphonate and camphor sulphonic acid (Pope, Chem. Soc. Proc. 1899, 15, 170; 1900, 16, 74; Pope and Harvey, Chem. Soc. Trans. 1901, 79, 74).

d-ac-Tetrahydro- β -naphthylamine d-bromo-camphor sulphonate, long colourless needles, m.p. 185° – 188° (decomp.), in absolute alcohol $[\alpha]_D = +86.5^\circ$; *l-ac-tetrahydro- β -naphthylamine l-bromo-camphor sulphonate*, colourless needles, m.p. 185° – 188° (decomp.), in absolute alcohol $[\alpha]_D = -86.2^\circ$.

In general, the optically active tetrahydro- β -naphthylamines undergo partial racemisation when liberated from their salts by soda and converted into other salts; *d-ac-tetrahydro- β -naphthylamine hydrochloride*, colourless needles, m.p. 243° – 245° , in aqueous solution $[\alpha]_D = +71.9^\circ$ and $[M]_D = +131.9^\circ$; *l-ac-tetrahydro- β -naphthylamine hydrochloride*, m.p. 243° – 245° , in aqueous solution $[\alpha]_D = -69.7^\circ$ and $[M]_D = -128^\circ$; *d-ac-tetrahydro- β -naphthylamine d-camphor sulphonate*, colourless needles or stout prisms $+\frac{1}{2}H_2O$, m.p. 210° – 211° , in aqueous solution $[\alpha]_D = +47.7^\circ$ and $[M]_D = +180.9^\circ$; *l-ac-tetrahydro- β -naphthylamine d-camphor sulphonate*, colourless scales $+H_2O$, m.p. 207° – 208° , in aqueous solution $[\alpha]_D = -9.7^\circ$ and $[M]_D = -36.8^\circ$ (the correct value should be $[M]_D = -68^\circ$, the low value obtained being due to contamination with the racemisation product of the *l*-base); *l-ac-tetrahydro- β -naphthylamine l-camphor sulphonate*, long transparent prisms $+\frac{1}{2}H_2O$, m.p. 210° – 211° , in aqueous solution $[\alpha]_D = -47.4^\circ$ and $[M]_D = -179.6^\circ$; *d-ac-tetrahydro- β -naphthylamine l-camphor sulphonate*, glistening scales $+H_2O$, m.p. 207° – 208° , in aqueous solution $[\alpha]_D = +13.3^\circ$ and $[M]_D = +50.4^\circ$; *d-ac-tetrahydro- β -naphthylamine platinichloride*, golden yellow scales practically insoluble in water, m.p. 240° (decomp.). *d-ac-Tetrahydro- β -naphthylamine* is a colourless oil and does not fume in the air. Racemisation takes place to a certain extent during its preparation, and the best specimen prepared consisted of 70 p.c. of *d*- and 30 p.c. of the *l*-base; *benzylidene-d-ac-tetrahydro- β -naphthylamine*, spherical aggregates of colourless needles, m.p. 58° – 60° , in absolute alcohol $[\alpha]_D = +27.6^\circ$; *benzoyl-d-ac-tetrahydro- α -naphthylamine*, felted needles, m.p. 155° – 157° , in acetone solution $[\alpha]_D = +58^\circ$; *d-ac-tetrahydro-aceto- β -naphthalide*, colourless needles, m.p. 104° – 106° , which exhibit triboluminescence when rubbed with a glass rod, in benzene solution $[\alpha]_D = +36.9^\circ$ (Pope and Harvey, *l.c.*). *ac-Tetrahydro- β -naphthylamine d-methylene-camphor*, glistening nearly colourless plates, m.p. 141° – 144° (Pope and Read, Chem. Soc. Trans. 1909, 95, 180).

In order to ascertain the relative rotatory effects of the aromatic and alicyclic rings, Frankland and Ormerod (Chem. Soc. Trans. 1903, 83, 1342) compared the rotation of tartaro-di- α -naphthylamide, tartaro-di- β -naphthyl-

amide, tartaro-di- α -tetrahydro- β -naphthylamide, and tartaro-di- α -tetrahydro- β -naphthylamide in pyridine solution. It was found that the rotatory effect of the naphthalene nucleus varies greatly (*a*) according to whether it is attached to the aminic nitrogen by the α - or β -carbon atom, and (*b*) according to which ring of the tetrahydronaphthalene nucleus is reduced. The molecular rotation of tartaro-di- α -tetrahydro- β -naphthylamide is less than that of β -naphthylamide itself, but greater than that of tartaro-*p*-toluidide, whilst the molecular rotation of tartaro-di- α -tetrahydro- β -naphthylamide is even less than that of either tartaro-methylamide or ethylamide. *Tartaro-di- α -tetrahydro- β -naphthylamide*, needles, m.p. 186° , in pyridine solution $[\alpha]_D = +205.9^\circ$ and $[M]_D = +840^\circ$; *tartaro-di- α -tetrahydro- β -naphthylamide*, white microcrystalline solid, m.p. 221° , in pyridine solution $[\alpha]_D = +58.9^\circ$ and $[M]_D = +240^\circ$ (Frankland and Ormerod, *l.c.*).

Hilditch (Chem. Soc. Trans. 1911, 99, 229), from measurements made with neutral camphorates in alcoholic solution, and camphor sulphonates in chloroform solution, showed very clearly the enhancing effect of an aromatic group as contrasted with the very small effect of the hydroaromatic nucleus. A benzenoid group, when united to another unsaturated group, enhances optical activity, and the preponderating factor is its unsaturated nature, the ring structure having very little to do with its influence on rotatory power. Conclusions which are comparable with these were drawn by von Auwers (Ber. 1913, 46, 2991) in the case of the dihydronaphthalenes with regard to other optical properties.

ac-Tetrahydro- β -naphthol was first resolved into its optically active components by Pickard and Littlebury (Chem. Soc. Trans. 1906, 89, 1254), using *l*-menthyl-carbimide, but this method did not result in the preparation of the two optically active isomerides in a state of purity. Pickard and Kenyon (Chem. Soc. Trans. 1912, 101, 1427) prepared the isomerides in a pure condition by fractional crystallisation of the brucine and cinchonidine salts of the hydrogen phthalate of *ac-tetrahydro- β -naphthol*.

ac-Tetrahydro- β -naphthol hydrogen phthalate, large prisms, m.p. 90° – 92° ; *l-cinchonidine salt* of the *hydrogen phthalate* of *l-ac-tetrahydro- β -naphthol*, needles, m.p. 168° – 169° , in ethyl alcoholic solution $[\alpha]_D = -71.16^\circ$; *l-brucine salt* of the *hydrogen phthalate* of *d-ac-tetrahydro- β -naphthol*, m.p. 109° – 112° , in ethyl alcoholic solution $[\alpha]_D = +4.79^\circ$; *l-ac-tetrahydro- β -naphthol hydrogen phthalate*, needles, m.p. 94° – 96° , in ethyl alcoholic solution $[\alpha]_D = -9.67^\circ$; *d-ac-tetrahydro- β -naphthol hydrogen phthalate*, needles, m.p. 94° – 96° , in ethyl alcoholic solution $[\alpha]_D = +9.76^\circ$; *l-ac-tetrahydro- β -naphthol*, large prismatic needles, m.p. 50° , b.p. $141^\circ/17$ mm., in chloroform solution $[\alpha]_D = -67.1^\circ$; *d-ac-tetrahydro- β -naphthol*, large prismatic needles, m.p. 50° , b.p. $141^\circ/17$ mm., in chloroform solution $[\alpha]_D = +67.1^\circ$; *l-ac-tetrahydro- β -naphthylphenyl carbamate*, feathery needles, m.p. 119° , in chloroform solution $[\alpha]_D = -26.31^\circ$.

A number of esters of *l*- and *d*-*ac-tetrahydro-*

β -naphthol have been prepared by heating the alcohol with a slight excess of the anhydride of the acid at 110°–120° for 6 hours, and form strongly refractive oils with slight but fragrant odours.

1-*ac*-Tetrahydro- β -naphthyl acetate, b.p. 149°/18 mm.; 1-*ac*-tetrahydro- β -naphthyl propionate, b.p. 158°–159°/18 mm.; d-*ac*-tetrahydro- β -naphthyl n-valerate, b.p. 169°/11 mm.; 1-*ac*-tetrahydro- β -naphthyl n-heptoate, b.p. 191°–193°/14 mm.; d-*ac*-tetrahydro- β -naphthyl n-nonoate, b.p. 195°–197°/5 mm.; d-*ac*-tetrahydro- β -naphthyl laurate, m.p. 35°–36°, b.p. 218°/3 mm. (Pickard and Kenyon, *l.c.*); Pickard and Neville (Chem. Soc. Trans. 1905, 87, 1763; Chem. Soc. Proc. 1905, 31, 257) isolated *dextro*- Δ^2 (or Δ^3)-dihydro- α -naphthoic acid, colourless felted needles, m.p. 103°, in chloroform solution $[\alpha]_D = +212.9^\circ$ and $[M]_D = +370.4^\circ$, and showed that its transformation into the Δ^1 -acid in the presence of bases proceeds as a unimolecular reaction (*cf.* Pickard and Yates, Chem. Soc. Trans. 1906, 89, 1484); 1-menthyl-d- Δ^2 (or Δ^3)-dihydro- α -naphthoate, prismatic needles, m.p. 150°, in ethyl alcoholic solution $[\alpha]_D = +75.06^\circ$ (Pickard and Neville, *l.c.*). Pickard and Yates (Chem. Soc. Trans. 1906, 89, 1101) resolved the tetrahydronaphthoic acids into their optically active components; 1-menthylamine 1-*ac*-tetrahydro- α -naphthoate, large glassy prisms, m.p. 123°, in absolute alcoholic solution $[\alpha]_D = -29.35^\circ$ and $[M]_D = -97.1^\circ$; 1-*ac*-tetrahydro- α -naphthoic acid, colourless glistening plates, m.p. 52.5°, in chloroform solution $[\alpha]_D = -15.95^\circ$ and $[M]_D = -28.07^\circ$; 1-menthylamine d-*ac*-tetrahydro- α -naphthoate, rhombic crusts, m.p. 78° (not sharp), in absolute alcoholic solution $[\alpha]_D = -12.79^\circ$; d-*ac*-tetrahydro- α -naphthoic acid, m.p. 49°–50°, was not quite pure, in chloroform solution $[\alpha]_D = +14.01^\circ$; 1-menthylamine 1-*ac*-tetrahydro- β -naphthoate, rhombic prisms, m.p. 150°, in absolute alcoholic solution $[\alpha]_D = -55.17^\circ$ and $[M]_D = -182.6^\circ$; 1-*ac*-tetrahydro- β -naphthoic acid, prismatic needles, m.p. 99°, in chloroform solution $[\alpha]_D = -51.82^\circ$ and $[M]_D = -91.2^\circ$; d-*ac*-tetrahydro- β -naphthoic acid, prismatic needles, m.p. 99°, in chloroform solution $[\alpha]_D = +40.35^\circ$ (Pickard and Yates, *l.c.*; *cf.* Rupe, Annalen, 1903, 327, 157).

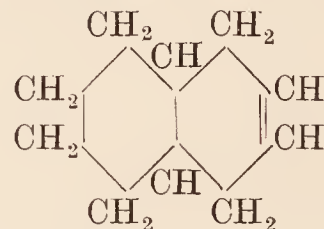
Hexahydronaphthalene is formed by heating naphthalene with hydriodic acid (b.p. 127°) and phosphorus for 55 hours at 245° (Wreden and Znutowicz, J. Russ. Phys. Chem. Soc. 1876, 8, 149; *ibid.* 9, 183; Ber. 1876, 9, 1606). It is prepared in a yield of 80 p.c. by heating 67 parts of naphthalene with 95 parts of hydriodic acid (b.p. 127°) and 30 parts of red phosphorus for 9 hours at 240°–250° (Graebe and Guye, Ber. 1883, 16, 3028; *cf.* Agrestini, Gazz. chim. ital. 1883, 12, 495; Ber. 1883, 16, 796).

Hexahydronaphthalene is a colourless fragrant liquid, b.p. 204°–205°/764 mm. (Agrestini), or 199.5°–200° (Graebe and Guye), or 199.5°–200.5° (Lossen and Zander, Annalen, 1884, 225, 111), or 197° (Wreden and Znutowicz); sp.gr. 0.952 at 0° (Wreden and Znutowicz); for refractive power, *see* Nasini and Bernheimer (Gazz. chim. ital. 1886, 15, 84), and Pellini (Gazz. chim. ital. 1901, 31, i. 1); for heat of combustion, *see* Leroux (Compt. rend. 1910, 151, 384).

Sulphonation with fuming sulphuric acid yields two isomeric *disulphonic acids*, which are separated by treating their *potassium salts* with boiling alcohol, in which one is soluble and the other insoluble. The crystals of the former are anhydrous, while those of the latter contain $1\frac{1}{2}$ molecules of water of crystallisation; both of the salts when fused with potassium hydroxide yield α -naphthol. When hexahydronaphthalene is treated with bromine in molecular proportions, a violent reaction occurs with evolution of hydrogen bromide, and the product is, apparently, a *monobromodihydronaphthalene*, nearly colourless oil, heavier than water, b.p. 269°–270°.

A mixture of *hexahydronaphthalenes*, b.p. 75°–85°/15 mm., was obtained by Borsche and Lange (Annalen, 1923, 434, 219) by heating dichlorodecahydronaphthalenes, b.p. 148°–150°/18 mm., with aniline. These react with bromine to form a mixture of *hexahydronaphthalenetetrabromides* of m.p. 184° and 200°, respectively.

Octahydronaphthalene.—Hydrocarbons of the formula $C_{10}H_{16}$ have been prepared directly or indirectly by the hydrogenation of naphthalene, but the products described by various workers vary considerably in their physical properties and in the nature of their derivatives. Thus, Wreden and Znutowicz (J. Russ. Phys. Chem. Soc. 1876, 8, 149; *ibid.* 9, 183; Ber. 1876, 9, 1606) obtained an *octahydronaphthalene*, b.p. 187°, sp.gr. 0.910 at 0°, by heating a mixture of 5 grms. of naphthalene, 9 grms. of hydriodic acid (b.p. 127°) and red phosphorus at 260°–265° for about 15 hours. Leroux (Compt. rend. 1905, 140, 590; *ibid.* 141, 953; Ann. Chim. 1910, [8] 21, 458) obtained *A*-octahydronaphthalene, a colourless liquid becoming yellow in air, b.p. 190°–192°, sp.gr. 0.921 at 0°, and 0.914 at 17°, n_D 1.499, by heating decahydro- α -naphthol with potassium hydrogen sulphate. This compound readily reacts with bromine forming the corresponding *dibromodecahydronaphthalene*, colourless prisms, m.p. 143°. On the other hand, decahydro- β -naphthol, when heated with anhydrous oxalic acid, phosphoric oxide, zinc chloride and sodium hydrogen sulphate at 200°, yields *B*-octahydronaphthalene, to which Leroux attributes the constitution



colourless mobile liquid, b.p. 190°–192°, sp.gr. 0.910 at 0°, and 0.901 at 13°, n_D 1.491. It combines with nascent hydrogen iodide and with organic acids, whilst it reacts so readily with bromine to form uncrystallisable polymerides that cooling and dilution are necessary. When brominated in chloroform solution with the theoretical quantity of bromine it forms a mixture of *B*-dibromodecahydronaphthalene, needles or large prisms, m.p. 85°, which Borsche and Lange (Annalen, 1923, 434, 219) have shown to be a derivative of trans-decahydronaphthalene, and an *isomeride*, m.p. 41°, which Leroux considers to be the trans-dibromide. *B*-octahydronaphthalene reacts with formic acid at 175° to form

the formic ether of decahydro- β -naphthol, identical with the product obtained by the direct etherification of decahydro- β -naphthol.

Ipatiew (Ber. 1910, 43, 3386), by treating decahydro- β -naphthol (b.p. 243°–248°) with hydrogen under a pressure of 40 atmospheres at 358° for 10 hours in the presence of alumina, obtained *octahydronaphthalene*, b.p. 197°–199°, which on treatment with hydrobromic acid yields a *hydrobromide*, b.p. 95°–100°/20 mm., whilst bromination in alcoholic ethereal solution results in the formation of a crystalline *dibromide*, m.p. 169°. Borsche and Lange (Annalen, 1923, 434, 219) by heating *cis*-decahydro- β -chloronaphthalene with aniline obtained pure *cis*-2-*octahydronaphthalene*, b.p. 72°–73°/15 mm., which forms a *dibromide*, m.p. 170°. Collie (Chem. Soc. Trans. 1893, 63, 337) obtained *octahydrodimethylnaphthalene*, b.p. 210°–215°, by reducing 3 : 3'-dimethyl-2-aceto-1 : 1'-dinaphthol with hydriodic acid at 180°.

Decahydronaphthalene.—The products obtained by the action of hydriodic acid on naphthalene are dependent upon the temperature and the duration of heating, and di-, tetra-, hexa- and octahydronaphthalenes have been formed in this manner. Finally, Wreden and Znatowicz (Bull. Soc. Chim. 1876 [2], 26, 449; J. Russ. Phys. Chem. Soc. 1876, 8, 149; Annalen, 1877, 187, 164) have shown that hexahydrocymene, $C_{10}H_{20}$, and decahydronaphthalene, $C_{10}H_{18}$, are obtained in a similar manner. Berthelot, who studied this reaction, assigned the formula $C_{10}H_{22}$ to the first of these hydrocarbons, and considered the second to be diethylbenzene, $C_{10}H_{14}$. The decahydronaphthalene obtained by Wreden differs in its physical properties from decahydronaphthalene obtained by Leroux (Compt. rend. 1904, 139, 672; Ann. Chim. 1910 [8], 21, 458), who did not know of the existence of *cis*- and *trans*-forms of decahydronaphthalene, by the direct hydrogenation of naphthalene, or better, of tetrahydronaphthalene at 160° in the presence of a nickel catalyst formed by the reduction of its oxide at 250°. Ipatiew (Ber. 1907, 40, 1287) prepared decahydronaphthalene by the action of hydrogen on naphthalene under 178 atmospheres pressure at 230° for 12 hours in the presence of nickel oxide as catalyst; Willstätter, Hatt and King (Ber. 1912, 45, 1474; *ibid.* 1913, 46, 527) found that an ethereal or glacial acetic acid solution of naphthalene readily absorbs hydrogen in the presence of platinum black with the formation of decahydronaphthalene, but the latter is not formed until the whole of the naphthalene has been converted completely into tetrahydronaphthalene. When Willstätter and Seitz (Ber. 1923, 56, 1388) re-examined this process it was found, however, that the particular hydrogenation product obtained is dependent on the oxygen content of the catalyst. Skita and Meyer (Ber. 1912, 45, 3592) obtained decahydronaphthalene by the use of colloidal platinum and gum arabic in glacial acetic acid solution. Wimmer (D. R. PP. 300052, 302488, 1915) obtained a suitable catalyst by the reduction of dry nickel formate, either alone or made into a paste with an oil or a saturated glyceride, and found that decahydronaphthalene was produced when hydrogenation was effected in its presence under a pressure of 15 to 30

atmospheres at a temperature of 180°–200°. Zelinski (Ber. 1923, 56, 1723) prepared decahydronaphthalene smoothly by passing tetrahydronaphthalene and hydrogen over platinised asbestos at 150°–160°, or over palladium black at 120°. Decalin (decahydronaphthalene) is manufactured technically by a continuation of the hydrogenation described for the manufacture of tetralin (p. 763). The hydrogenation is best effected in two stages, and the further reduction of tetrahydronaphthalene is carried out in a second autoclave containing a fresh catalyst. Four hours are required for the conversion of 1 kg. of tetralin to decalin under a constant hydrogen pressure of 12–15 atmospheres. In order to remove small quantities of tetralin or other impurities, the product is digested with small quantities of sulphuric acid, separated from resinified products, washed, dried and distilled (Schroeter, etc., Annalen, 1922, 426, 12). Lower hydro-derivatives, such as tetra-, hexa-, and octahydronaphthalene can be removed from decalin by treatment with liquid sulphur dioxide, in which the latter is insoluble (Tetralin, G.m.b.H., D. R. P. 310781, 1917; *cf.* Inoue, J. Chem. Ind. Japan, 1923, 26, 1316).

Decalin is a colourless oil, b.p. 189°–191°/770 mm., setting-point -125° , d_4^{18} 0.8842, and is unaffected by exposure to air (Schroeter).

Decahydronaphthalene is a colourless oil with an odour of menthol, volatile with steam, b.p. 187°–188° (Leroux), or b.p. 189°–191° (Ipatiew), or b.p. 190°–191°/720 mm. (Willstätter, &c.), or b.p. 190.4°–191.2°/764 mm. (von Auwers, Ber. 1913, 46, 2988), sp.gr. 0.893 at 0°, 0.877 at 20°, n_D 1.46 (Leroux), d_4^{20} 0.894 (von Auwers), molecular heat of combustion at constant pressure 1503.9/19.2° (Roth and von Auwers, Annalen, 1915, 407, 145; *cf.* Leroux, Compt. rend. 1910, 151, 384). The following are some of the more recently determined constants: m.p. $-124^\circ \pm 2^\circ$; b.p. 191.7°; vapour pressure formula

$$\log p = -2395.2/T + 1.75 \log T - 0.00270983T + 4.62719;$$

heat of vaporisation 71.01 cal./gr.; Trouton constant 21.1; ebullioscopic constant 6036; specific heat (15°–18°) 0.395; density

$$d_t = 0.8975(1 - 818 \times 10^{-6}t);$$

coefficient of expansion (15°–25°) 0.00086; critical temperature 724°; surface tension at b.p. 15.71 dynes/cm.; molecular surface energy 505.1 (Herz and Schuftan, Zeitsch. physikal. Chem. 1922, 101, 259). The *trans*- and *cis*-forms of decahydronaphthalene have been described by Hückel (Nach. K. Ges. Wiss. Göttingen, 1923, 43), who considered that all preparations of decahydronaphthalene are mixtures of the *cis*- and *trans*-forms, the product obtained with platinum black containing about 90 p.c. of the *cis*- and 10 p.c. of the *trans*-form. Willstätter and Seitz (Ber. 1924, 57, 683), however, found that various preparations made with platinum consisted of the pure *cis*-form, whereas hydrogenation of naphthalene with nickel and hydrogen at 160°–162° gave mainly the *trans*-form. *trans-Decahydronaphthalene* has b.p. 185°/753 mm.; d_4^{20} 0.872;

n_D^{20} 1.47009. *cis-Decahydronaphthalene* has b.p. 193° ; d_4^{20} 0.898; n_D^{20} 1.48279. Decahydronaphthalene does not form a picrate. It is oxidised by acid permanganate to phthalic acid, and is also attacked by ozone (Koetschau and Flemming, Zeit. f. angew. Chem. 1924, 37, 42). When decahydronaphthalene is boiled with aluminium chloride, a mixture of saturated hydrocarbons, $C_{10}H_{18}$, b.p. 157° – 250° , is obtained (Boedtker and Rambech, Bull. Soc. chim. 1924, [iv.] 35, 631).

Decahydronaphthalene is chlorinated readily forming monochlorodecahydronaphthalene, colourless liquid, colouring rapidly on exposure to light, b.p. 112° – $115^\circ/18$ mm., and dichlorodecahydronaphthalene, b.p. 145° – $148^\circ/18$ mm. (Leroux, l.c.). Borsche and Lange (Annalen, 1923, 434, 219) found, however, that when decahydronaphthalene is chlorinated corresponding with the introduction of one chlorine atom, only 25 p.c. of 2-chloro-decahydronaphthalene, b.p. 121° – $122^\circ/18$ mm., is formed, and that this is, moreover, a mixture of *cis*- and *trans*-forms. When this mixture is heated with aniline a mixture of octahydronaphthalenes, b.p. 76° – $80^\circ/15$ mm. is obtained.

cis-Decahydro- β -chloronaphthalene, obtained from *cis*-decahydro- β -naphthol, has b.p. 110° – $112^\circ/15$ mm., but the *trans*-isomeride, from *trans*-decahydro- β -naphthol, has not been obtained pure. The decahydronaphthalene chlorination mixture contains *dichlorodecahydronaphthalenes*, b.p. 148° – $150^\circ/18$ mm., converted by heating with aniline into hexahydronaphthalenes, b.p. 75° – $85^\circ/15$ mm.

Decahydronaphthalene does not react with bromine at the ordinary temperature, whilst at higher temperatures dehydrogenation occurs with the formation of brominated naphthalene derivatives (Leroux, l.c.).

Ipatiew (Ber. 1907, 40, 1287) obtained decahydro- α -naphthol by heating α -naphthol in the presence of nickel oxide as catalyst with hydrogen under a pressure of 168–172 atmospheres at a temperature of 225° – 230° for 72 hours. Leroux (Compt. rend. 1905, 141, 953; Ann. Chim. 1910, [8] 21, 458) found that decahydro- α -naphthol is formed also by hydrogenation after the method of Sabatier and Senderens in the presence of reduced nickel. In this case the reactivity of the catalyst has an important bearing upon the nature of the product. Thus, with freshly reduced nickel the reaction is complicated by dehydrogenation, and the formation of the corresponding ketone, which is obtained readily in the presence of reduced copper, also occurs when nickel is used. For the production of decahydro- α -naphthol, Leroux found that the hydrogenation is best effected in two stages. Incomplete hydrogenation of the naphthol is first effected at 170° , and the mixture obtained is then further hydrogenated at a temperature of 135° at the rate of about 10 grms. per day, the yield under all conditions being very low.

Decahydro- α -naphthol forms fine colourless needles, volatile with steam, m.p. 62° , b.p. $109^\circ/12$ mm., or $230^\circ/\text{atm.}$ (Leroux); m.p. 57° – 59° , b.p. 245° – 250° (Ipatiew). It forms a gelatinous sodium salt; *acetate*, colourless mobile oil of fruity odour, b.p. $127^\circ/18$ mm.; *benzoate*, lamellæ,

m.p. 68° ; *phenylcarbamate*, thin needles, m.p. 172° .

Decahydro- β -naphthol was obtained by Leroux (l.c., and Compt. rend. 1905, 140, 590) by the repeated hydrogenation of β -naphthol at a temperature of 150° as described in the case of the β -isomeride, and also by Ipatiew (l.c.), by heating β -naphthol with hydrogen under a pressure of 191 atmospheres for 72 hours at 225° , or for 56 hours at 230° in the presence of nickel oxide as catalyst. *Decahydro- β -naphthol* forms needles, volatile with steam, m.p. 75° , b.p. $115^\circ/13$ mm., or $230^\circ/\text{atm.}$ with decomposition (Leroux), or m.p. 99° – 100° , b.p. 242° – 244° (Ipatiew). Decahydro- β -naphthol forms on *acetate*, colourless liquid, b.p. $120^\circ/12$ mm., or $250^\circ/\text{atm.}$; *formate*, b.p. $126^\circ/20$ mm., or 245° decomp./atm., obtained by keeping a mixture of decahydro- β -naphthol and formic acid for 24 hours; *benzoate*, fine needles or prisms, m.p. 48° ; *ethyl ether*, colourless liquid, b.p. 100° – $102^\circ/12$ mm., obtained by the action of ethyl iodide on sodium decahydro- β -naphtholate; *phenylcarbamate*, needles which sublime at 160° and melt at 165° .

The product obtained by Ipatiew was examined by Mascarelli (Atti R. Accad. Lincei, 1911, (v), 20, ii. 223; Mascarelli and Recusani, Gazz. chim. ital. 1912, 42, ii. 35), who found it to consist of two components, flat transparent crystals, m.p. 75° , and colourless prismatic crystals, m.p. 105° . It was considered that four different decahydro- β -naphthols may exist, forming two pairs of enantiomorphs, and these two products were regarded as the two corresponding racemic mixtures. Hüchel (Nach. K. Ges. Wiss. Göttingen, 1923, 43), however, considers that the assumption that these products have the hydroxyl groups in *cis*- and *trans*-positions is erroneous, for he obtained different products on oxidising them. Oxidation of the decahydro- β -naphthol, m.p. 105° , gives a decalone (keto-derivative) having d_4^{20} 1.005, whilst the decahydro- β -naphthol, m.p. 75° , gives a decalone having d_4^{20} 0.975. Oxidation of the decahydro- β -naphthol, m.p. 105° , with alkaline potassium permanganate gives a mixture of the *cis*-form of 2-carboxycyclohexane-1-propionic acid and the *cis*-form of cyclohexane-1:2-diacetic acid, whereas the decahydro- β -naphthol, m.p. 75° , gives a mixture of the *trans*-form of 2-carboxycyclohexane-1-propionic acid and the *trans*-form of cyclohexane-1:2-diacetic acid. The hydrogenation of *ac-tetrahydro- β -naphthol* gives *cis-decahydro- β -naphthol*, m.p. 105° , which is converted on oxidation into *cis-decahydro- β -naphthalone*, b.p. $247^\circ/755$ mm., d_4^{21} 1.0039, n_D^{21} 1.4918 (*semicarbazone*, m.p. 182° – 183° ; *oxime*, viscid oil). *trans-Decahydro- β -naphthol*, m.p. 75° , is converted on oxidation into *trans-decahydro- β -naphthalone* (*semicarbazone*, m.p. 192° – 193° ; *oxime*, m.p. 75°).

Cis - 2 : 3 - dihydroxydecahydronaphthalene, needles or polygonal plates, m.p. 160° , is formed by boiling B-dibromodecahydronaphthalene with aqueous potash; by the action of aqueous potash on the iodohydrin derived from B-octahydronaphthalene; or by the action of water, alkalis, dilute sulphuric acid (1:4) or dilute acetic acid (1:15) on decahydronaphthylene-

2:3-oxide; *diacetate*, needles, m.p. 85°; *diphenyl-urethane*, needles, m.p. 195°. When B-octahydronaphthalene is acted upon by nascent hypoiodous acid it yields the *iodohydrin* of *cis*-2:3-*dihydroxy-decahydronaphthalene*, needles or prismatic crystals, m.p. 70°. When the iodohydrin in dry ethereal solution is treated with finely powdered potash for about 2 days at the ordinary temperature *decahydronaphthylene-2:3-oxide* is obtained. It is a fairly mobile colourless liquid with an agreeable odour. When B-dibromodecahydronaphthalene in acetic acid solution is boiled with silver acetate, a mixture of the acetates of *cis-trans*-2:3-*dihydroxy-decahydronaphthalene* with *cis*-2:3-*dihydroxy-decahydronaphthalene* is formed. This mixture when hydrolysed with alkalis yields a crystalline product, m.p. 120°, which, on crystallisation from benzene, may be separated into *trans*-2:3-*dihydroxydecahydronaphthalene*, needles or long prisms, not volatile with steam, m.p. 141°, and *cis-trans*-2:3-*dihydroxydecahydronaphthalene*, which has a constant melting-point of 125°, even after numerous recrystallisations. *Trans*-2:3-*dihydroxydecahydronaphthalene* forms a *diacetate*, viscous liquid, b.p. 152°/18 mm.; *diphenyl-urethane*, small crystals, m.p. 121°. The mixture of *cis-trans*-2:3-*dihydroxy-decahydronaphthalene* (m.p. 125°), on treatment with acetic anhydride, yields a mixture of acetates which can be separated into the acetates of its components. Both of these stereoisomeric glycols on careful oxidation with acid permanganate yield a *product*, $C_{10}H_{16}O$, m.p. 167° (Leroux, Compt. rend. 1909, 148, 1614; Ann. Chim. 1910, [8] 21, 458).

The decahydronaphthyl ketones are obtained during the hydrogenation of the corresponding naphthols in the presence of nickel, but they are more conveniently prepared by the oxidation of decahydro- α - and β -naphthol.

Decahydro- α -naphthyl ketone, prismatic tables, m.p. 32°, is obtained by oxidising decahydro- α -naphthol with chromic acid in acetic acid solution, the crude product being purified by conversion into its bisulphite compound. It forms an *oxime*, long needles which sublime at 100° and melt at 165°, which on treatment with warm dilute sulphuric acid immediately regenerates the ketone in a pure condition, whilst on reduction with sodium and absolute alcohol it yields decahydro- α -naphthylamine; *semicarbazone*, white needles, m.p. 230°, and a crystalline *phenylhydrazone* which rapidly decomposes on exposure to air (Leroux, Compt. rend. 1907, 144, 981; Ann. Chim. 1910 [8], 21, 458).

Decahydro- β -naphthyl ketone, prepared in a similar manner to the α -isomeride, is a colourless liquid of unpleasant odour, b.p. 110°/15 mm. or 240°/atm., sp.gr. 0.988 at 0° and 0.979 at 16°, n_D 1.4834. It forms a *bisulphite* compound, small nacrcous lamellæ, slightly decomposed by boiling water; *semicarbazone*, needles, m.p. 195°; an unstable *phenylhydrazone*; *oxime*, small colourless prisms, m.p. 76°. Decahydro- β -naphthyl ketone when treated with sodium and absolute alcohol or with hydriodic acid in the presence of zinc is converted into decahydro- β -naphthol, and there is no trace of the formation of a stereoisomeride (Leroux, Compt. rend. 1905, 141, 46; Ann. Chim. 1910, [8] 21, 458).

Decahydro- β -naphthyl ketone readily condenses with ethyl chloroacetate to form a *glycidic ester*, colourless, slightly viscous oil, b.p. 148°–150°/4 mm., which is readily hydrolysed to the corresponding *acid*, a very viscous liquid. Distillation of this acid under reduced pressure yields *decahydro- β -naphthaldehyde*, colourless, mobile liquid, b.p. 95°–96°/3 mm.; *semicarbazone*, m.p. 178°–179°. Similarly, the ketone, when condensed with ethyl chloropropionate, yields *ethyl decahydro- β -naphthyl methyl glycidate*, colourless mobile liquid, b.p. 155°–156°/4 mm., which, on hydrolysis, is converted into the corresponding *acid*, fine needles, m.p. 149°–150°. This acid is more stable than its lower homologue, and on distillation it yields *decahydro- β -naphthyl methyl ketone*, mobile liquid of camphoraceous odour, b.p. 94°–95°/3 mm.; *semicarbazone*, m.p. 240°–241° (Darzens and Leroux, Compt. rend. 1912, 154, 1812).

Decahydro- α -naphthylamine, colourless liquid of disagreeable odour, b.p. 96°–97°/14 mm., is obtained by reducing the oxime derived from decahydro- α -naphthyl ketone with sodium and absolute alcohol. It is a very powerful base, which absorbs carbon dioxide from the air; *hydrochloride*, prismatic crystals, m.p. 190° (decomp.); *platinochloride*, needles; *picrate*, prismatic crystals, m.p. about 240° (decomp.); *acetyl derivative*, long needles which sublime at 125° and melt at 182°; *benzoyl derivative*, needles which sublime at 150° and melt at 195° (Leroux, Compt. rend. 1907, 144, 981; Ann. Chim. 1910, [8] 21, 458).

Decahydro- β -naphthylamine, prepared in a similar manner to the α -isomeride, is a colourless liquid of unpleasant odour, b.p. 112°/15 mm. It is a strong base and absorbs carbon dioxide from the air; *hydrochloride*, small colourless prisms; crystalline *picrate*, m.p. 203°–204°; *acetyl derivative*, small needles, m.p. 173°. Neither of the decahydro-amines possesses any mydriatic properties (Leroux, Compt. rend. 1905, 141, 46; Ann. Chim. 1910, [8] 21, 464).

Decahydro- β -naphthoic acid is formed together with decahydronaphthalene by the prolonged reduction of sodium β -naphthoate with hydrogen under 119 atmospheres pressure at 360° in the presence of nickel oxide as catalyst (Ipatiew, Ber. 1909, 42, 2100), and by the further reduction of ar-tetrahydro- β -naphthoic acid with sodium and amyl alcohol (von Braun, Kirschbaum and Schuhmann, Ber. 1920, 53, 1161). It melts at 79°–81° (Ipatiew), or 79° (von Braun, &c.), and boils at 190°–192°/21 mm. (von Braun, &c.).

Borsche and Lange (Annalen, 1923, 434, 219), however, prepared a Grignard reagent from the mixture of 2-chlorodecahydronaphthalenes, b.p. 121°–122°/18 mm., which, on treatment with carbon dioxide, etc., gave a mixture of *cis*- and *trans*-decahydronaphthalene 2-carboxylic acids, separable through the amides.

cis-Decahydronaphthalene 2-carboxylic acid is a resin, b.p. 150°/15 mm. (*amide*, m.p. 165°–166°; *anilide*, needles, m.p. 128°–130°), and *trans-decahydronaphthalene 2-carboxylic acid* melts at 103° (*amide*, m.p. 195°; *anilide*, needles, m.p. 155°–158°).

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TETRAHYDROPALMATINE. In the course of the preparation of corydaline from the rhizomes of *Corydalis cava*, Spaeth, Mosetlig,

Trothandl (Ber. 1923, 56, [13] 875; through J. Pharm. Chim. 1924, 29, 450) have isolated two bases, *dextro*-tetrahydropalmatine, $C_{21}H_{25}O_4N$, and *dextro*-corypalmine. Tetrahydropalmatine occurs in colourless crystals, m.p. 142° ; $\alpha_D + 292.5^\circ$ in EtOH solution. Corypalmine is found among the phenolic bases. It forms small colourless crystals, m.p. 236° – 237° ; $\alpha_D + 280^\circ$ in $CHCl_3$ solution (Pharm. J. 1924, 113, 45).

TETRAHYDROXYBENZENE *v.* PHENOL AND ITS HOMOLOGUES.

TETRAIODOPYRROLE *v.* IODOLE.

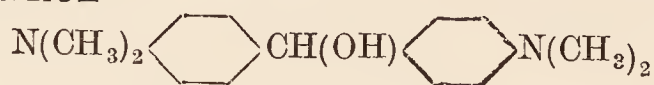
TETRAKETONES *v.* KETONES.

α -TETRALONE. Syn. for α -ketotetrahydronaphthalene. For dyes derived from this substance, *v.* Herzog and Kreidl, Ber. 1922, 55, [B.] 3394.

TETRAMETHYLAPIONAL *v.* PHENOL AND ITS HOMOLOGUES.

TETRAMETHYLBENZENES *v.* CYMENES.

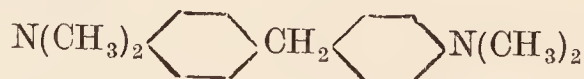
4 : 4' - **TETRAMETHYLDIAMINO BENZ-HYDROL**



is best obtained by oxidising tetramethyldiaminodiphenylmethane with lead peroxide (Möhlman and Heinze, Ber. 1902, 35, 359). May also be prepared by reducing tetramethyldiaminobenzophenone with zinc-dust in an alkaline solution of amyl alcohol (Bad. Anil. and Soda Fabrik. D. R. P. 27032), m.p. 96° , soluble in alcohol or ether.

TETRAMETHYLDIAMINO BENZOPHENONE (Michler's ketone) *v.* KETONES.

4 : 4' - **TETRAMETHYLDIAMINODIPHENYLMETHANE**



Prepared by treating dimethylaniline with hydrochloric acid and formaldehyde, heating on the water-bath and adding caustic soda. The excess of dimethylaniline is removed by steam distillation when the tetramethyldiaminodiphenylmethane crystallises on cooling, m.p. 91° , b.p. 390° . On sulphonation it yields the corresponding monosulphonic acid.

TETRAMETHYLDIAMINOTHIOPHENONE *v.* KETONES.

TETRAMETHYLHYDROXYBENZENE *v.* PHENOL AND ITS HOMOLOGUES.

TETRAMETHYLSAFRANINE *v.* AZINES.

TETRAMINE. A toxin obtained from *Actinia equina*. The syrupy aqueous extract of the plant was purified by tannic acid after slightly acidifying with phosphoric acid. The precipitate produced with phosphotungstic acid was separated into three silver fractions and a lysine fraction, the last named containing the toxin. This was purified by means of the picrate and obtained as chloride by evaporation with alcoholic hydrogen chloride, and recrystallised from hot absolute alcohol. The aurichloride $C_4H_{12}N \cdot AuCl_4$, forms yellow needles, the chloroplatinate $(C_4H_{12}N)_2PtCl_6$, orange-yellow octahedra, sparingly soluble in water, insoluble in absolute alcohol; the picrate



long needles. The chloride $C_4H_{12}NCl$ is very hygroscopic, is easily soluble in hot alcohol, sparingly in cold, is optically inactive, and cannot be further methylated by methyl sulphate. The toxin must therefore be tetramethylammonium hydroxide, $N(CH_3)_4OH$, and produces the typical curare-like physiological effect, and in large doses quickly causes death by paralysis (D. Ackermann, F. Holtz, and H. Reinwein, Zeitsch. Biol. 1923, 79, 113–120; Chem. Zentr. 1923, 94, 111, 1283; J. Soc. Chem. Ind. 1923, 42, 1245 A).

TETRANITRODIMETHYLANILINE. Pure dimethylaniline (100 kilos.) is run slowly, with continuous stirring and cooling, into 1000 kilos of sulphuric acid, free from lead. If the dimethylaniline is added too fast, or the cooling is insufficient, the solution and the resulting product are dark-coloured. Nitric acid (430 kilos.) is run into an enamelled iron water-jacketed nitrating vessel and warmed to 44° . The sulphuric acid solution of dimethylaniline is slowly run in and the temperature maintained below 44° . When two-thirds of the dimethylaniline have been added, the temperature is allowed to rise to 53° or 55° . The injection takes from 8 to 9 hours, and the mixture is kept stirred for two hours longer to ensure complete nitration. Tetranitrodimehtylaniline crystallises only from the acid, the size of the crystals depending upon the strength of the nitric acid employed. The product is filtered off, washed free from acid, and crystallised from pure benzene, 550 kilos. being dissolved in, say, 1850 litres of benzene. The yield is 87 p.c. and the m.p. of the pure product is 129° to 130° (Langenscheidt, Z. ges. Schiess-u-Sprengstoffw, 1912, 7, 445; J. Soc. Chem. Ind. 1912, 31, 1147).

TETRATHIONIC ACID *v.* SULPHUR.

TETRAZO- COMPOUNDS *v.* DISAZO- AND TETRAZO- COMPOUNDS.

TETRODOTOXIN $C_{16}H_{31}NO_{16}$ (?), a poisonous substance found in the ovaries of some species of fish (*Tetrodonæ*), used as food in Japan. A white hygroscopic powder; only slightly soluble in water, insoluble in practically all organic solvents. Is precipitated from its aqueous solutions by metallic oxides. Appears to be neither an alkaloid nor a protein. Dilute hydrochloric acid converts it into a basic substance and a nitrogen-free crystalline product. Fatal dose (subcutaneous injection), 4 mgrms. per kilo. of body weights (Tahara, Biochem. Zeitsch. 1910, 30, 255.)

TETRONAL (diethyldisulphonedimethylmethane or ethyl sulphonol) $(C_2H_5)_2C(SO_2C_2H_5)_2$ is prepared like sulphonol from diethyl ketone and ethyl mercaptan (Baumann and Kast, Zeitsch. physiol. Chem. 14, 61; D. R. P. 49366; Frdl. 1887–1890, ii. 523). It forms colourless, odourless, glistening leaflets, or radiating almost round fibrous groups similar to urea oxalate; m.p. 85° , soluble in 450 parts of cold water, but more readily soluble in boiling water, in alcohol, and in ether. It is employed in medicine as a substitute for sulphonol.

Adulteration of tetronal and trional with sulphonol, which is cheaper than the two former, may be detected by treating the suspected sample with ether, in which sulphonol is much less soluble, the residue will, therefore, contain

sulphonal which may be detected by its melting-point and its known reactions (Gabutti, J. Pharm. Chim. 1907, 25, 183); *v.* SULPHONAL.

TETRYL (explosive). *Trinitrophenyl-methylnitroamine*, see EXPLOSIVES. In order to obtain tetryl pure enough without recrystallisation to pass the British Government specification test, the dimethylaniline treated must be free from mineral matter. Continuous sampling at all stages of the operation is necessary. The nitrous fumes volatilised in the process are recovered as calcium nitrate by washing the gases from the nitrators with milk of lime. The solution so obtained is treated with manganese sulphate, and the manganese nitrate produced isolated and heated to yield fuming nitric acid. Manganese dioxide remains and is reconverted into the sulphate and used again. The spent acid is de-nitrated and the nitric acid obtained concentrated in a similar way (W. L. Tanner, Chem. and Met. Eng. 1923, 29, 404; J. Soc. Chem. Ind. 42, 1923, 1104 A).

Commercial samples of tetryl are often found to contain occluded acid. In view of the fact that the vacuum heat test for tetryl is becoming the standard test, a knowledge of its comportment with concentrated sulphuric acid may have considerable bearing on the interpretation of this test. When tetryl is heated in capryl alcohol or *n*-butyl alcohol, methylpicramide is

formed in small quantities. Tetryl is not affected by prolonged boiling with dilute sulphuric acid, but with aqueous chromic acid it yields picric acid. In the presence of glacial acetic acid, tetryl is destroyed by chromic acid. It is rapidly dissolved by concentrated sulphuric acid at 100°, forming a red solution. The tetryl is re-precipitated on pouring this solution on ice. If the solution is allowed to stand for some days and then poured on ice, a gummy material is precipitated which dissolves in warm alcohol. The solution deposits crystals of methylpicramide in 20 p.c. yield of the theoretical. As methylpicramide on nitration yields tetryl the reaction is thus shown to be reversible (T. L. Davis and C. F. H. Allen, J. Amer. Chem. Soc. 1924, 46, 1063; J. Soc. Chem. Ind. 1924, 43, B. 539).

For a bibliography and summary of existing knowledge of tetryl, especially as regards its manufacture and military application, see L. Desvergues (Mém. Poudres, 1922, 19, 217-268). The author describes and compares the French, British, and German methods of manufacture, and concludes that the first is, on the whole, the best. Experiments on the effects on the various properties of tetryl, of keeping it at different temperatures for longer and shorter periods, are described in J. Soc. Chem. Ind. 1923, 42, 205 A.

END OF THE SIXTH VOLUME.



